RELATIONSHIPS BETWEEN ANALOGOUS ORGANIC COMPOUNDS OF SILICON AND CARBON

HENRY GILMAN

Department of Chemistry, Iowa State College, Ames, Iowa

AND

G. E. DUNN

Department of Chemistry, University of Manitoba, Winnipeg, Canada

Received November 13, 1952

CONTENTS

I. INTRODUCTION

The synthesis of the first organosilicon compound, tetraethylsilane, in 1863 (52) led to the hope that there might exist a whole new branch of chemistry in which silicon would take the place of carbon (54, 205). 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.

The most careful and extensive series of investigations known in organosilicon chemistry—the fundamental series upon which the whole modern "silicone" technology rests—was begun by F. S. Kipping about 1900 with this point in 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 forty-year 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 (111). Later workers have tended to confirm this viewpoint.

Nevertheless, 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 (111), 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 (202) and many of their papers drew attention to the contrast between the reactions 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 in the body of this review.

The 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. When the conclusions are those of the original worker, this has been indicated by some suitable statement in the report. In other cases the authors have drawn comparisons between the results of workers in the organosilicon field and those of other workers in purely organic chemistry.

A glance at recent works on organosilicon chemistry (32, 149, 155) will make it obvious that all the literature references to analogous compounds of silicon and carbon could be recorded only in a 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. The nomenclature used has been that recommended by the committee on nomenclature of the American Chemical Society (144), along with certain well-established trivial terminology.

II. PHYSICAL PROPERTIES

From the relative positions of silicon and carbon in the Periodic Table, the following facts can be derived: (*a*) both have a normal covalence of 4; (*b*) both have their normal bonding directed tetrahedrally; (*c*) silicon is larger and heavier than carbon; (*d*) silicon is less electronegative than carbon; and (*e*) under favorable circumstances silicon may have a coördination number greater than 4. The similarities between the compounds of carbon and silicon will be considered in the light 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 a large part upon relationships (a) and (b) show striking similarities. Some of these may be illustrated here.

As is stated by relationship (a), the normal covalence of both elements is 4. 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 4, while in the free radicals, such as triphenylmethyl, carbon has a formal covalence of 3. In consequence of relationship (b), compounds in which four different groups are attached to either element show optical activity (111).

A. Density and boiling point

In figure 1 the densities of about twenty organosilicon compounds are plotted against the densities of the analogous carbon compounds. It is seen that there is a reasonably good linear relationship represented by the equation $S = 0.118 + 0.878C$, where S is the density of a silicon compound and C is that of its carbon analog.

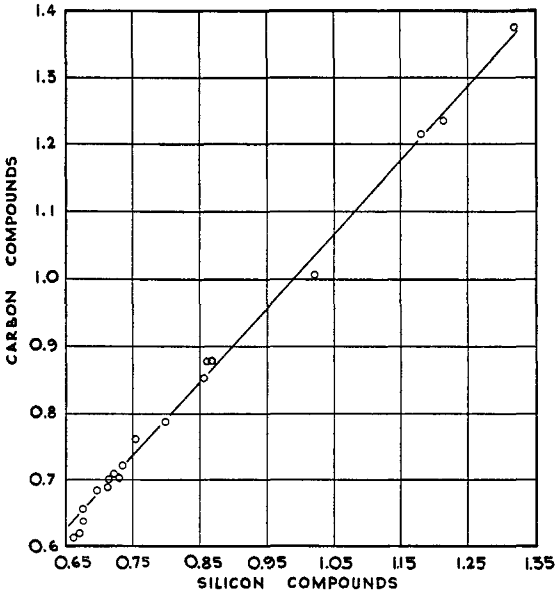


FIG. 1. Relationship between the densities of organosilicon compounds and the densities of their carbon analogs.

Lewis and Newkirk (123) have shown that an additive system of atomic and group boiling-point numbers developed by Kinney (101–105) for carbon compounds can be extended to organosilicon compounds. This suggests that a linear relationship like that for densities should apply to the boiling points of silicon and carbon analogs, and such is found to be the case. The relationship is represented by the equation $S = 19.8 + 0.878C$. Since Trouton's Rule has been shown to hold with about the same accuracy for silicon compounds as for carbon compounds (1, 18, 43, 47, 49, 50), it is apparent that a similar relationship must hold for molar heats of vaporization.

B. Refractive index

In the case of molar refractions the situation is not so simple. Warrick (198) and Sauer (161) 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 (35) 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. 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 1.4–1.6, a satisfactory test can be made by comparing analogous refractive indices. The meager data available are plotted in figure 2.

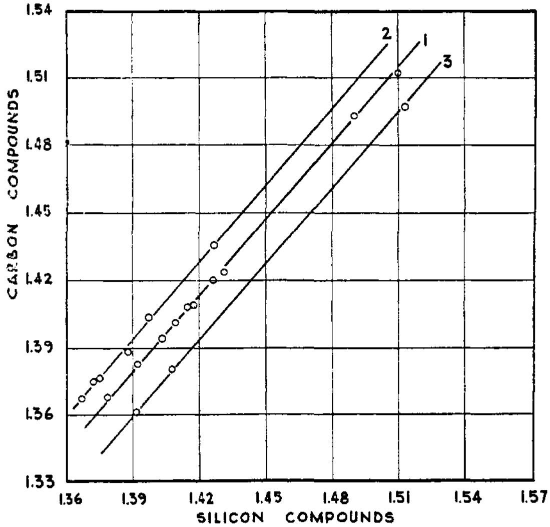


FIG. 2. Relationship between the refractive indices of organosilicon compounds and the refractive indices of their carbon analogs. The points on line 1 represent compounds in which silicon is bonded only to carbon; the compounds of line 2 have one silicon–carbon bond replaced by a silicon–oxygen bond; those of line 3 have one silicon–carbon bond replaced by a silicon–hydrogen bond.

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 $S = 0.193 + 0.870C$. Compounds containing silicon–oxygen and silicon–halogen bonds fall on separate straight lines parallel to the first, and what data there are suggest that compounds having silicon–hydrogen and silicon–nitrogen bonds also fall on parallel lines. These plots show clearly that the change in molecular refractivity effected by the introduction of a given atom into an organosilicon molecule depends to a marked extent on whether the new atom is attached to carbon or to silicon. This is striking evidence for the validity of the postulate by Denbigh (35) and Warrick (198) that bond refractivities are more generally applicable than atomic refractivities. Refraction of visible light depends upon the electronic polarizability of molecules, and for any atom this will vary as other atoms of different size and electronegativity are attached. Evidently, relationship (d) is of importance in comparing refraction by silicon and carbon analogs.

C. Melting points

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 crystal structure, with consequent erratic effect upon melting-point relationships. This is found to be true. 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°C., as compared to a probable error of 5°C. in the boiling-point calculation.

D. Surface tension

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 the surface tension of various organosilicon compounds have led to atomic parachors for silicon varying from 25.8 to 38.2 (37, 51, 92, 93, 99, 129), and several authors have suggested that bond parachors might be more satisfactory (129). This indicates that a comparison of surface tensions of silicon and carbon analogs might lead to a result more like that for the refractive index than like those for the boiling point and density.

E. Viscosity

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 (51) to a coiled-chain structure for polysiloxanes which uncoils with rising temperatures, thus offsetting the usual decrease in viscosity with increasing temperature. The smaller size of the carbon atom prevents coiling of the polyisobutylene molecules. On the other hand, Barry concludes from their respective relationships between viscosity and molecular weight that the amount of coiling is about the same in polysiloxanes and polyisobutylenes (5).

F. Bond properties

The bond energy of a bond A—B is defined as $1/n$ times the heat of formation at 0°K. and zero pressure of the gas AB_n from its elements in the gaseous state. The concept of additive bond energies was introduced by Fajans (45) and extended by Pauling (146), whose empirical values for bond energies were for several years the commonly accepted ones. These values were calculated from thermochemical data, taking the heats of atomization of the elements to be: C, 124; Si, 85.0; H, 51.7; O, 59.1; N, 85.1; F, 31.8; Cl, 28.9; Br, 26.9; I, 25.6 kcal./mole. Since the publication of Pauling's values further work has been done on most of these heats of atomization, and the current estimates are as follows: C, 170; Si, 102; H, 52.0; O, 59.2; N, 136; F, 18.9; Cl, 29.0; Br, 26.7; I, 25.5. The new values for hydrogen, oxygen, chlorine, bromine, and iodine, based on the spectroscopic dissociation energies of their diatomic molecules (173), are essentially the same as the earlier ones, but the values for carbon, silicon, nitrogen, and fluorine have been drastically revised and are still in doubt. The heat of atomization of carbon is particularly controversial. Direct and various indirect measurements give varying values which fall into three main groups centering around 124 (88, 126), 140 (46, 84), and 170 (80) kcal./mole. We have chosen the highest of the three possibilities, since the majority of recent investigations favor that value, and for various other reasons which will be discussed later. The silicon value is in even greater doubt. Pauling's figure was based on a somewhat dubious direct measurement (16) and the value chosen here is actually twice the silicon–silicon bond energy approximated from the activation energy of the thermal decomposition of disilane (173). Recent studies of the heats of atomization of nitrogen and fluorine agree that the old values for nitrogen were too low and those for fluorine too high. From the various slightly differing values proposed we have chosen those favored by Glockler (80) and by Doescher (39), respectively.

The bond energies calculated using these revised heats of atomization are shown in column 2 of table 1. The corresponding values as originally reported by Pauling (146) are shown in parentheses below the revised ones. The principal reason for favoring the new values over the old is that they are in better agreement with experimental bond dissociation energies (36, 182, 190). The dissociation energy of a bond A—B is defined as the difference in energy between the compound AB_n and the fragments $AB_{n-1} + B$. For a diatomic molecule the bond dissociation energy will be equal to the bond energy, but for a polyatomic molecule this will not be true. In the latter case the bond dissociation energy will be equal to the bond energy *plus* any energy changes which occur when the fragments reorganize after the fission (190, 196). Consequently, the A—B bond dissociation energy will be different for each B, as B's are successively removed, and no one of these energies need equal the bond energy. Since all ordinary carbon and silicon compounds are polyatomic, it is not to be expected that the bond energies of column 2 of table 1 should be equal to the bond dissociation energies of column 3, which correspond to the removal of the first atom or group from a molecule. However, there is reason to suppose that, while the bond energy should be different from this bond dissociation energy, it should not be greatly different (36, 182). Consequently, the bond dissociation energies listed in table 1 are considered to favor the newer values for bond energies.

Although the newer values are higher than the old (except for fluorine bonds), it will be seen that qualitatively the energies of analogous bonds to silicon and

TABLE 1

Properties of analogous bonds to carbon and silicon

ELEMENT	BOND ENERGY(a)		BOND DISSOCIATION(b) ENERGY		ATOMIC ELECTRONEGATIVITY(c)	PER CENT IONIC CHARACTER(d)		BOND LENGTH(e)	
	C	Si	C	Si		C	Si	C	Si
	kcal./mole	*kcal./mole*	*kcal./mole*	*kcal./mole*				Å.	Å.
C	84.9 (58.6)	75.0(f) (57.6)	83	79(g)	2.5	0	11	1.54(c)	1.93(c)
Si	75.0(f) (57.6)	51.0 (42.5)	79(g)	51(h)	1.8	11	0	1.93(c)	2.34(i)
H	98.1 (87.3)	79.9 (75.1)	101		2.1	4	3	1.09(j)	1.49(j)
O	80.9(k) (70.0)	106(l) (89.3)	90		3.5	23	51	1.43(c) (1.42)	1.61(m) (1.74)
N	81.9(n) (48.6)				3.0	6	30		
F	102 (107)	134 (143)			4.0	44	70	1.36 (1.37)	1.54 (1.69)
Cl	77.9 (66.5)	90.3 (85.8)	74		3.0	6	30	1.76 (1.73)	2.02 (2.05)
Br	66.4 (54.0)	73.5 (69.3)	68		2.8	3	22	1.91 (1.90)	2.19 (2.22)
I	52.1 (45.5)	55.0 (51.1)	54		2.5	0	8	2.12 (2.11)	(2.49)

(a) From the heats of atomization given on page 82 and the data of Skinner (173), except where otherwise noted. The values in parentheses are those of Pauling (146).

(b) From the review by Szwarc (190), except where otherwise noted.

(c) Pauling's values (146).

(d) From Pauling's relationship between electronegativity difference and partial ionic character (146).

(e) From Schomaker and Stevenson (165), unless otherwise noted. The values in parentheses are calculated from Schomaker and Stevenson's formula and radii. The radius for carbon was that of Gordy (83).

(f) From the heat of formation of carborundum (16) and the heats of atomization given on page 82.

(g) The activation energy of the thermal decomposition of tetramethylsilane (87). However, Waring (197) gives 50.5 and 46 kcal./mole for the activation energy of the thermal decomposition of tetraethyl- and tetrapropylsilanes, respectively, in a process which is claimed to involve no chain reactions.

(h) From the activation energy of the pyrolysis of disilane (173).

(i) Brockway and Davidson (24).

(j) Calculated from Pauling's covalent radii (146).

(k) Calculated from the heat of formation of dimethyl ether (16) and the heats of atomization on page 82.

(l) Calculated from the heat of formation of silica (16) and the heats of atomization on page 82.

(m) No data on organosilicon compounds are available; the value given is for quartz (128).

(n) Calculated from the heat of formation of methylamine (16) and the heats of atomization on page 82.

carbon still stand in the same relationships to each other; silicon forms weaker bonds with carbon, hydrogen, and silicon but stronger bonds with the more electronegative elements than does carbon. The only qualitative change in relationship which is significant for this review is that between the silicon–carbon and carbon–carbon bond energies. On Pauling's scale the energies of these bonds were essentially equal, while on the new scale the silicon–carbon bond is decidedly the weaker of the two. This new relationship is in better agreement with the results of pyrolysis of alkylsilanes than was the old. Decomposition begins at lower temperatures for tetramethyl-, tetraethyl-, and tetrapropylsilanes than for their carbon analogs, and the products indicate that the first bond to break is the carbon–silicon one in each case (87, 197).

TABLE 2

Heats of formation of organosilicon compounds (191)

COMPOUND	HEAT OF FORMATION		
	Observed	Calculated from Pauling's data	Calculated from the revised data*
	kcal./mole	*kcal./mole*	*kcal./mole*
$[(CH_3)_2SiO]_3$	356.5	353.5	421.9
$(C_2H_5)_2Si(OH)_2$	219.5	193.6	228.2
$(CH_3)_2Si(OC_2H_5)_2$	197.5	174.0	198.3
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$	240.6	203.6	226.7

* Approximating the heat of vaporization from Trouton's Rule.

The only other available data which might give a critical test of the relative strength of carbon–carbon and silicon–carbon bonds are the heats of combustion of organosilicon compounds shown in table 2 (191). However, the compounds chosen have such a large number of bonds to hydrogen and oxygen that carbon–silicon bond energies calculated from them turn out to be small differences between large numbers and consequently unreliable. As table 2 shows, either set of energy values fits the data equally well.

From his empirical bond energies Pauling calculated a table of atomic electronegativities using the relationship

$$x_A - x_B = 0.208\sqrt{\Delta_{AB} - \tfrac{1}{2}(\Delta_{AA} + \Delta_{BB})}$$

where x represents the electronegativity of the atoms and Δ the energy of the bonds indicated by the subscripts. Since the bond energies have been revised, it would be expected that new values for the atomic electronegativities would result. In fact, however, electronegativities calculated from the new bond energies do not differ from Pauling's original values by more than 0.1 unit, except in the case of fluorine where the new value is 3.7 as compared with 4.0. Since fluorine thermochemistry is still in a state of flux, and the electronegativity changes indicated for the other atoms involved in organosilicon work are trifling, there seems to be no reason to modify Pauling's original figures. These are quoted in table 1 and used for purposes of comparison throughout this review. From

Pauling's relationship between electronegativity and bond polarity the per cent ionic character of various bonds to silicon and carbon has been calculated and listed in table 1. The lesser electronegativity of silicon compared with carbon makes all of the bonds to silicon more polar than the corresponding bonds to carbon. Consequently, bonds to silicon are expected to be, and are, more reactive toward polar reagents than are analogous bonds to carbon.

Finally, column 6 of table 1 records the lengths of bonds between silicon, carbon, and the other atoms of importance in organosilicon chemistry. Silicon, an element in the second row of the Periodic Table, is larger than carbon; hence bonds to silicon are uniformly longer than analogous bonds to carbon. Consequently, groups in which carbon is replaced by silicon are larger and more open as a result of the substitution. It would be expected then, that steric effects in organosilicon compounds might be quite different from steric effects in the carbon analogs. An organosilicon substituent such as the trimethylsilyl group, $(CH_3)_3Si—$, is larger than its carbon analog, the *tert*-butyl group, $(CH_3)_3C—$; hence two trimethylsilyl groups on the same or adjacent carbon atoms might interfere to a greater extent than would two *tert*-butyl groups. On the other hand, within the substituent itself the methyl groups are farther from the central atom and from each other when attached to silicon than when attached to carbon, so that the trimethylsilyl group should be less subject to internal strains and more subject to external attack than the *tert*-butyl group. Experimental evidence bearing on these points will be considered in the following section on chemical properties.

III. CHEMICAL PROPERTIES

A. Silicon–carbon single bonds

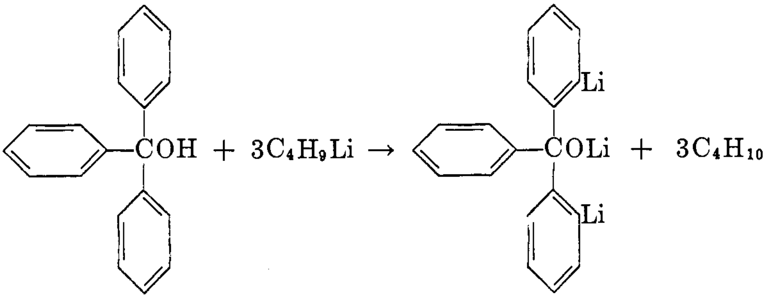
In comparing the chemical properties of organosilicon and carbon compounds, it should be noted that the strength of the bond between carbon and carbon (84.9 kcal./mole) is slightly greater than that between silicon and carbon (75.0 kcal./mole). It would be expected, in consequence, that toward homolytic cleavage the silicon–carbon bond should be slightly the more reactive. This is exemplified, as was previously indicated, by the greater ease of thermal decomposition of the tetraalkylsilanes (87, 197) compared to their carbon analogs. The difference is not great, however, and does not imply an instability of the carbon–silicon bond under ordinary conditions. Thus, such compounds as tetraphenylsilane (123) and tetraphenylmethane (195) can be boiled undecomposed at high temperatures (428°C. and 431°C., respectively) and are stable at temperatures of 500°C. and higher.

With regard to heterolytic cleavage, however, the situation is different. The fact that the silicon atom is larger, less electronegative, and capable of a greater maximum coördination number than the carbon atom makes the silicon–carbon bond considerably more reactive than the carbon–carbon bond toward a number of reagents.

For example, aryltrimethylsilanes are cleaved by acids under fairly mild conditions to give trimethylsilanol and a substituted benzene (71), while *tert*-butylbenzenes are relatively stable towards acids. Presumably the partial ionic character of the silicon–carbon bond facilitates attack by a proton at the negative (carbon) end of the dipole.

The silicon–carbon bond is also more susceptible to basic cleavage. Thus, benzyltriphenylsilane and many related compounds are readily cleaved by potassium hydroxide in alcohol, acetone, or dioxane, to give triphenylsilanol and a hydrocarbon (138), while benzyltriphenylmethane, for example, is relatively inert towards 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, Krieble and Elliott have pointed out that, 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 (122). In the case of trichloro(trichloromethyl)silane, cold water alone cleaves the carbon–silicon bond readily (37). In hexachloroethane the carbon–carbon bond is not cleaved even by alcoholic potassium hydroxide at 100°C. (14). 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 coördination number, all of which make nucleophilic attack easier.

These factors may be further illustrated by the reactions of the triarylcarbinols and triarylsilanols with *n*-butyllithium. When triphenylcarbinol is refluxed in ether with *n*-butyllithium two of the aromatic nuclei are metalated in the ortho position (62).



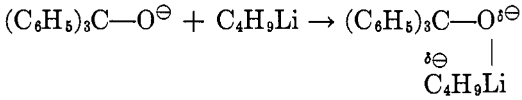
When triphenylsilanol is treated in the same way, one of the phenyl groups is displaced by *n*-butyl (60).

$$(C_6H_5)_3SiOH + 2C_4H_9Li \rightarrow (C_6H_5)_2Si(C_4H_9)OLi + C_6H_5Li + C_4H_{10}$$

p-Substituted triphenylsilanols are similarly cleaved, but tri-1-naphthylsilanol and most tetrasubstituted silanes are not. Metalation occurs only if the aromatic group contains an activating substituent, such as methoxyl. It is known that the first step in each case is the displacement of the hydroxyl hydrogen to give an oxyanion

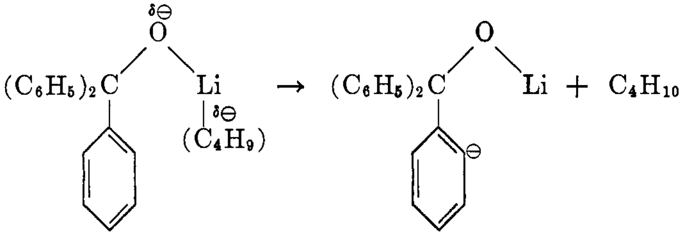
$$(C_6H_5)_3COH + C_4H_9Li \rightarrow (C_6H_5)_3CO^{\ominus}\ \ Li^{\oplus} + C_4H_{10}$$

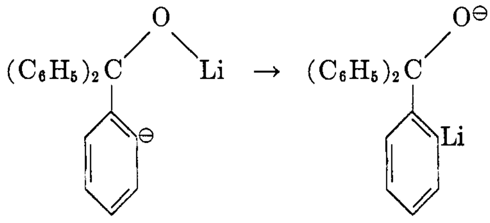
and it seems probable that the next step involves the coördination of the negatively charged oxygen with the positive (lithium) end of the *n*-butyllithium dipole.



$$(C_6H_5)_3C\text{—}O^{\ominus} + C_4H_9Li \rightarrow (C_6H_5)_3C\text{—}\underset{\overset{\delta\ominus}{C_4H_9Li}}{\overset{}{O^{\delta\ominus}}}$$

It may be supposed that the *n*-butyl group, which now has a partial negative charge, next attacks the most susceptible group. In the silanol case this is the silicon atom, because of its partial charge and its ability to expand its valence shell to accept more electrons. A phenyl group is displaced instead of oxygen, since the latter would have to be set free as a divalent oxide anion. In the carbinol case attack on the central carbon atom is hindered by the closer crowding of the phenyl groups around it, its inability to accept more than eight electrons into its valence shell, and the lesser ionic character of its bond to phenyl. Consequently, the butyl end of the *n*-butyllithium dipole attacks a proton from the ortho position of an adjacent ring.





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 (42). The relative susceptibilities of the silicon–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 (150), while with *tert*-butylbenzene aromatic bromination is possible (192).

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 (40, 174). Even anhydrous ferric chloride will cleave silicon–carbon bonds under mild conditions (131).

$$(C_2H_5)_4Si + FeCl_3 \xrightarrow[CHCl_3]{\text{reflux in}} (C_2H_5)_3SiCl + C_2H_6$$

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 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°C. to give triphenylmethane and benzene while, under similar conditions of pressure, tetraphenylsilane remains unchanged at temperatures as high as 450°C. (95). 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, where the shielding would be much reduced, is cleaved by hydrogen at 350°C. to triethylsilane and benzene (95). In the tetraarylmethanes the shielding of the central bonds is also good, but one may suppose that increased strains, due to the smaller central atom in the methane, make the central bonds unusually labile.

A similar effect is observed in the reactions of carbon–carbon and silicon–carbon bonds with the alkali metals. Many aryl-substituted ethanes are cleaved by sodium–potassium alloy to give organometallic compounds (3).

$$C_6H_5CH_2CH_2C_6H_5 + 2M \rightarrow 2C_6H_5CH_2M$$

It has recently been shown that silicon–carbon bonds, if sufficiently activated by aryl substituents, can be cleaved in a similar way (13).

$$(C_6H_5)_3SiC(CH_3)_2C_6H_5 + 2M \rightarrow (C_6H_5)_3SiM + C_6H_5C(CH_3)_2M$$

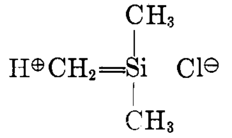
Although there is not enough evidence yet to warrant a definite conclusion, the indications are that silicon–carbon bonds are less readily cleaved than carbon–carbon bonds. If this is true, it is probably a result, at least in part, of the larger size of the silicon atom and the consequent reduced steric strains in silicon compounds.

B. 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 methylenediphenylsilane, $(C_6H_5)_2Si{=}CH_2$, from the hydrolysis of (chloromethyl)diphenylsilane (163). However, Kipping was unable to repeat this work, obtaining instead *sym*-dimethyltetraphenyldisiloxane (108). Fifteen years of research on the subject led him to the conclusion that "an ethylenic binding between carbon and silicon is either impossible or can only be produced under exceptional circumstances" (108, 114). 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, double bonds to second-row elements are unlikely because the greater bond distance makes the overlap of π-orbitals on the singly bonded atoms small (148). Mulliken has calculated quantum-mechanically the orbital overlap for bonds between elements of the first and second rows and reached the conclusion that the energies of first- and second-row double bonds should be about the same (142). A second-row single bond, however, according to his calculations, should be much stronger than a first-row single bond, so that, presumably, lack of silicon–carbon double bonds can 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. It must be noted, however, that all the evidence available to date indicates that the silicon–silicon single bond is weaker, not stronger, than the carbon–carbon single bond.

The lack of evidence for 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: $(CH_3)_4Si$, 1.93 Å.; $(CH_3)_3SiCl$, 1.89 Å.; $(CH_3)_2SiCl_2$, 1.63 Å.) (25, 26, 125), and it has been proposed (206) that this can be explained by increasing contributions from structures such as

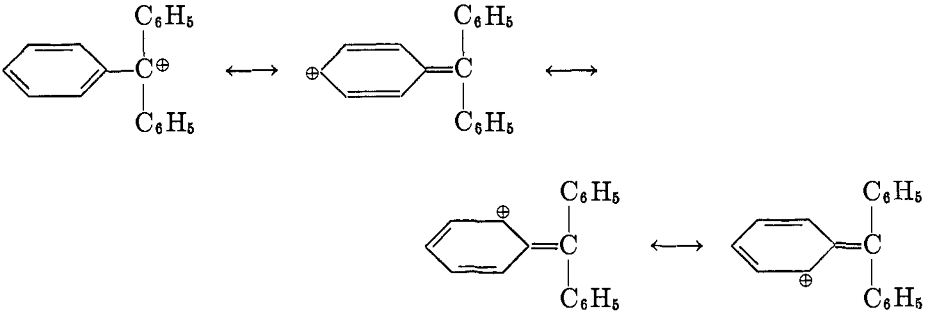


$$H^{\oplus}CH_2{=}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\quad Cl^{\ominus}$$

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 studies of the dipole moments of the halosilanes (33).

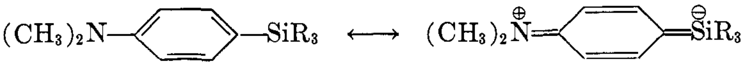
Pauling (146) points out that most double bonds are about 0.20 Å. shorter than the corresponding single-bond distances. Since the silicon–carbon bond distance in dichlorodimethylsilane is about 0.10 Å. shorter than in tetramethylsilane, the silicon–carbon bond in the former would be required by this theory to have about 50 per cent double-bond character. 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 compared with that lost by breaking a carbon–hydrogen bond and a silicon–chlorine bond. It seems probable, therefore, that an explanation for the silicon–carbon bond shortening as more halogens are attached to silicon is not to be found in a large amount of double-bond character of the silicon–carbon bond.

Such other evidence as is available indicates that contributions to the ground states of molecules by resonance structures having silicon doubly bonded to carbon are not large. For example, the absorption maxima in the ultraviolet of (*p*-dimethylaminophenyl)diphenylsilanol and tris(*p*-dimethylaminophenyl)-silanol were found to show no shift toward longer wave lengths in acid solution (65). In the analogous carbon compounds the corresponding shift is very pronounced, and is attributed to the formation of triarylcarbonium 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 the following



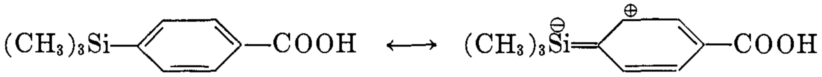
and to the reduction in steric strains brought about by the change from tetrahedral to planar configuration around the methyl carbon atom. The fact that the silanols exhibit no such shift is taken to indicate that siliconium ions are much less readily formed than are analogous carbonium ions. This is probably partly due 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.

Since silicon can expand its valence shell to accommodate more than eight electrons, an organosilicon compound has available to it a type of resonance interaction not possible for its carbon analog. For example, the ground state of a silicon compound containing the *p*-dimethylaminophenyl group might receive contributions from structures such as the following:



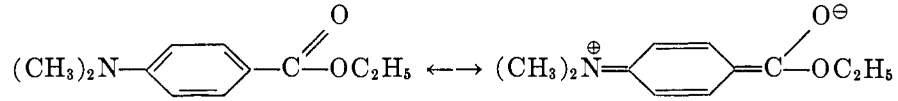
Several pieces of evidence indicate that these contributions are not important. Such structures are not possible in the corresponding carbon compounds, yet the ultraviolet absorption spectra of (*p*-dimethylaminophenyl)diphenylsilanol and tris(*p*-dimethylaminophenyl)silanol are remarkably similar to those of their carbon analogs (65). It seems unlikely, therefore, that the silicon compounds receive any important contributions from resonance structures not available to their carbon analogs.

Roberts, McElhill, and Armstrong studied the dissociation constants of the trimethylsilylbenzoic acids and the rates of reaction of these acids with diphenyldiazomethane (153). They found σ in Hammett's equation (85) to be -0.04 for the *p*-trimethylsilyl group and -0.12 for the *m*-trimethylsilyl group. The negative sign of both numbers indicates that the overall effect of the trimethylsilyl group is one of electron release toward the benzene ring; hence they conclude that contributions from structures such as



cannot be large.

Finally, a study of the rates of hydrolysis of triarylsilanes by mild alkali has shown that the σ-constant of the *p*-dimethylaminophenyl group is considerably less negative when obtained from the hydrolysis of silanes than when obtained from the hydrolysis of benzoic acid esters (66). This indicates a greater electron-releasing effect for the *p*-dimethylamino group when attached to the esters than when attached to the silanes. An explanation is found in the resonance interaction of the type



which has been shown to occur in the esters (199, 200) but evidently does not occur in the silanes.

These pieces of evidence taken together make it appear unlikely that organosilicon compounds receive significant contributions from resonance structures involving silicon–carbon double bonds.

C. 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 (32). 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. Thus, in contrast to the inertness of methane, silane is a spontaneously inflammable gas which is hydrolyzed readily by water and even more readily by aqueous acids and bases (184). Halogen acids react with it to give mixtures of halosilanes and hydrogen (130).

From the data of table 1 it is seen that the silicon–hydrogen bond is weaker than the carbon–hydrogen bond, although not strikingly so. 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. 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. In polarity the silicon–hydrogen bond is more like the carbon–halogen than the carbon–hydrogen bond and, as a result, many of the reactions of silanes resemble reactions of alkyl halides. For example, trialkylsilanes react with sodium ethoxide to give trialkylethoxysilanes and sodium hydride (134), a reaction which recalls the Williamson synthesis of ethers from alkyl halides rather than any reaction of tertiary hydrocarbons. Furthermore, Price has shown that the effects of substitution on rates are the same in this reaction as in nucleophilic displacements on alkyl halides and has proposed that the same mechanism applies to both (151).

This reactivity of the silicon–hydrogen bond decreases as the hydrogens of silane are successively replaced by alkyl or aryl groups (118). Thus, while hydrolysis of monoalkylsilanes by alkali is very rapid in a two-phase system (185), the hydrolysis of trialkylsilanes by alkali is comparatively slow, even in solution (151). Similarly, the bromination of silane is a violent reaction even at low temperatures (183), while the bromination of triphenylsilane takes place only slowly in refluxing carbon tetrachloride (10, 77). 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 chlorosilane (96):

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

No such reaction is known for carbon–hydrogen bonds, although anhydrous aluminum chloride catalyzes the analogous reaction of alkyl halides with both silicon–hydrogen (201) and carbon–hydrogen bonds (9). In another example, lithium di-*n*-butylamide reacts with triphenylsilane to give (di-*n*-butylamino)-triphenylsilane and lithium hydride (69), while no such reaction is known in carbon chemistry.

Triphenylsilane (72) and triethylsilane (134) also react with organolithium compounds in a similar way,

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

while triphenylmethane reacts with organolithium compounds in the reverse manner (79).

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

There is no report of an organolithium compound reacting with a tertiary aliphatic hydrocarbon in any manner.

In their reactions with alkali metals, however, triarylsilanes and triarylmethanes are more nearly alike. Triphenylmethane when heated with potassium metal gives triphenylmethylpotassium (86),

$$(C_6H_5)_3CH + K \rightarrow (C_6H_5)_3CK$$

and triphenylsilane behaves similarly with sodium–potassium alloy in ether (12).

$$(C_6H_5)_3SiH + NaK \rightarrow (C_6H_5)_3SiK + NaH$$

On the other hand, triphenylmethane is not reported to react with the less reactive metal lithium, while triphenylsilane with lithium gives hexaphenyldisilane (67).

$$2(C_6H_5)_3SiH + 2Li \rightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + 2LiH$$

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 coworkers reported that chloroform, under the influence of organic peroxides or ultraviolet light, adds to olefins to give 1,1,1-trichloroalkanes (100). Almost immediately several authors (6, 30, 179) reported a similar reaction of trichlorosilane.

$$Cl_3SiH + CH_2{=}CHR \xrightarrow{\text{peroxide or ultraviolet light}} Cl_3SiCH_2CH_2R$$

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 from 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 somewhat surprising that this series of reactivities does not parallel the bond energies (Si—H, 79.9; C—Cl, 77.9; Si—Cl, 90.3; C—H, 98.1 kcal./mole) in a case where, *a priori*, they might be expected to do so.

D. *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 (149).

From the data of table 1 it will be noted that the silicon–silicon bond has only about one-half the bond energy of the carbon–carbon bond. This difference has sometimes been held responsible for the extreme scarcity of polysilanes as compared to carbon chains (154). The weakness of the silicon–silicon bond is undoubtedly a factor in this disparity of numbers, but it seems unlikely that the scarcity of silicon–silicon chain compounds can be traced entirely to lack of thermal stability. Thus, 1,2-diethyl-1,2-diphenyl-1,2-dipropyldisilane boils undecomposed at 268°C./100 mm. (107), hexaphenyldisilane melts undecomposed at 355°C. (164) and, even though octaphenylcyclotetrasilane is very slowly transformed to a clear plastic mass on prolonged heating above 400°C., this does not result in carbonization or loss of weight and decomposition sets in only at higher temperatures (113). Unsubstituted disilane and trisilane undergo thermal decomposition at 311°C. and 319°C., respectively (186). 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.

The reactivity of the silicon–silicon bond likewise does not account for the small number of compounds known. Although polysilanes are cleaved by alkali in a manner not recorded for carbon chains, disilanes are not cleaved by hot concentrated sulfuric acid (31), refluxing aqueous or alcoholic alkali (107), oxygen in boiling xylene (64), sodium in boiling xylene (164), or iodine in boiling chloroform (77). In fact, toward alkali metals the hexaaryldisilanes are *less* reactive than their carbon analogs. Thus, hexaphenylethane is easily cleaved by sodium or sodium amalgam (3), while hexaphenyldisilane is not attacked by these reagents and requires potassium (76), sodium in liquid ammonia (77), or sodium–potassium alloy to effect cleavage (76). 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 (116). The same reagent did not attack disilanes or octadecamethylcyclohexasilane (29, 116). The latter was decomposed only by alkali in boiling cyclohexanol (29).

The lack of polysilanes may be traced largely to the lack of suitable methods of preparation rather than to instability of the products. The great majority of methods for building carbon–carbon chains depends ultimately on some form of unsaturation, and unsaturated silicon compounds are not known. Consequently, 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. Using the Wurtz method, Kipping has prepared two isomeric octaphenyltetrasilanes (115), and Burkhard has prepared a dodecamethylcyclohexasilane (29). Until recently these and some of their derivatives were the only known organic compounds containing more than one silicon–silicon bond. Completely halogenated straight-chain silanes containing as many as twenty-four silicon–silicon bonds are known (170, 171), but when these are treated with Grignard reagents the products do not contain more than one silicon–silicon bond (168). This ease of cleavage of completely halogenated silicon atoms does not indicate any great instability of the silicon–silicon bond, however, for it is paralleled by the lability of completely halogenated carbon atoms—in the haloform reaction, for example.

It is now possible to modify the basic Wurtz-type synthesis by preparing silylpotassium compounds, R_3SiK, and coupling them with halosilanes (13, 76). By this procedure it is possible to build up chains of silicon atoms in a stepwise manner. Thus far, compounds containing two and three silicon–silicon bonds have been prepared and found to be reasonably stable (78).

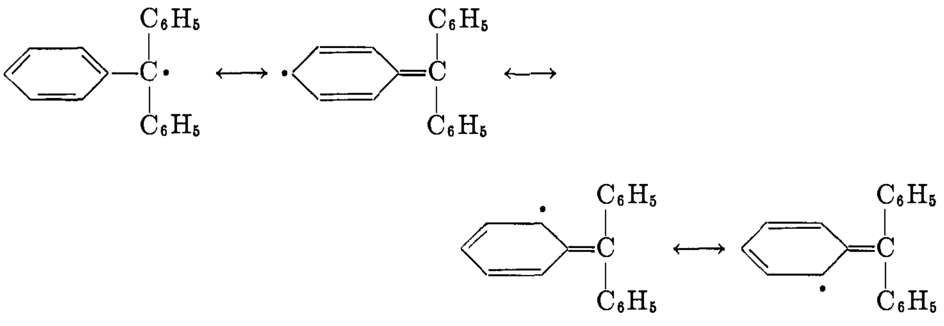
$$(C_6H_5)_3SiK + (C_6H_5)_2SiCl_2 \begin{array}{l} \nearrow (C_6H_5)_3SiSi(C_6H_5)_2Si(C_6H_5)_3 \\ \\ \searrow (C_6H_5)_3SiSi(C_6H_5)_2Cl \end{array} .$$

$$2(C_6H_5)_3SiSi(C_6H_5)_2Cl + 2Na \rightarrow (C_6H_5)_3Si[Si(C_6H_5)_2]_2Si(C_6H_5)_3$$

Indeed, they are more stable than their carbon analogs, for they show no tendency to dissociate into free radicals.

In this one respect at least, the silicon–silicon bond shows a stability 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 (164). Since the silicon–silicon bond energy is only about one-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. This is not true, however. The three reported hexaaryldisilanes, hexaphenyldisilane (164), hexa-*p*-tolyldisilane (168), and hexa-*p*-biphenylyldisilane (67), are stable in air, melt undecomposed at temperatures above 350°C., and do not react with oxygen, iodine, or other reagents which are quickly attacked by triarylmethyl radicals.

Two factors may be of importance in this difference. First, the steric strains involved in the disilanes must be considerably smaller than in the corresponding carbon compounds, owing to the larger size of the silicon atoms. Consequently, the tendency to dissociate must be reduced in the disilanes. However, when attempts are made to introduce greater strains in the disilanes by introducing more bulky groups, the reactions are unsuccessful. Thus, when chloro(tri-*o*-tolyl)silane (74) or chloro(tri-1-naphthyl)silane (61) is treated with 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 (74). This is to be contrasted with the reported facile preparation of tri-*o*-tolylmethyl from chloro(tri-*o*-tolyl)methane and mercury (193). Evidently the steric factors in these cases are great enough to prevent Wurtz-type coupling, so the failure of the reaction $R_3SiCl + Na \rightarrow R_3Si\cdot + NaCl$ to occur must be due to some other factor. It is suggested (193) that 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 the highly hindered triarylchlorosilanes do not react with sodium have



been 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 (193).

E. Silicon–silicon double bonds

To date, only two compounds have been suggested to contain silicon–silicon double bonds. These are:

$C_2H_5(C_6H_5)Si{=}Si(C_6H_5)C_2H_5$ (110) and $[(C_6H_5)_3Ge]_2Si{=}Si[Ge(C_6H_5)_3]_2$ (139)

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.

F. Silicon–halogen bonds

The halosilanes 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 synthesized 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 (167). In the second, silicon or silicon alloy is treated with a halogen acid to give tetrahalosilanes, trihalosilanes, and dihalosilanes (166). In the third, silicon or a silicon alloy is treated with an alkyl or aryl chloride at a high temperature to give mixtures of mono-, di-, and trialkyl- or triarylchlorosilanes (156). Bromides are conveniently prepared by analogous methods (166) but iodides not so readily (55, 57). Fluorides are usually prepared from the chlorides by reaction with metal fluorides (19, 20, 21, 158). None of the direct syntheses work with carbon, except the combination of carbon and fluorine (136).

The physical data available for the silicon–halogen and carbon–halogen bonds are recorded in table 1. There has been a good deal of discussion of these properties in the literature, and the subject is still a debatable one. Pauling's (146) 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 structures as $\overset{\oplus}{Cl}{=}\overset{\ominus}{Si}Cl_3$. Since the carbon atom cannot expand its valence shell, the shortening in the case of carbon tetrafluoride was explained in terms of structures such as $\overset{\oplus}{F}{=}CF_2\overset{\ominus}{F}$, which might also be of importance in the silicon case.

Later, Schomaker and Stevenson (165) emphasized that some shortening of all heteropolar bonds is due to the partial ionic character of the bond (due not to the above structures, but to the ordinary ionic structures $Cl_3\overset{\oplus}{Si}\ \ \overset{\ominus}{Cl}$) 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 1 the bond distances calculated on this basis are given in parentheses. The experimental values are those not in parentheses.

Still more recently, Pitzer (148) 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, owing 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 (142) have given some support to this theory.

Recently other authors (34, 58) 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 the similar homolytic cleavage of the silicon–chlorine bond. This has been discussed previously under silicon–hydrogen bonds.

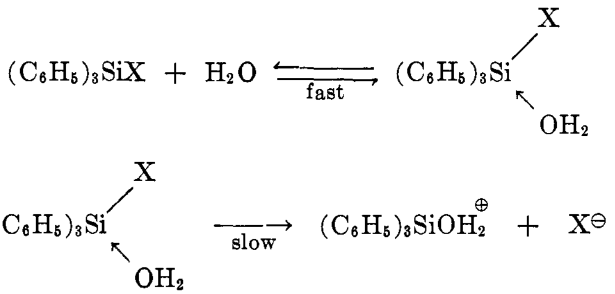
Toward polar reagents the silicon halides are uniformly more reactive than their carbon analogs. This difference is most evident in their relative ease of hydrolysis. Thus, while carbon tetrachloride and chloroform are stable toward aqueous solvents, silicon tetrachloride and trichlorosilane are hydrolyzed rapidly, even by moist air (56).

The ease of hydrolysis of silicon halides decreases as the halogen atoms are successively replaced by alkyl or aryl groups (32, 42). In the carbon series the reverse is probably true (91), 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 effects of substituents are undoubtedly due to different mechanisms of hydrolysis. It is well established that the trityl halides hydrolyze by the S_N1 mechanism,

$$(C_6H_5)_3CX \xrightleftharpoons{\text{slow}} (C_6H_5)_3C^{\oplus} + X^{\ominus}$$

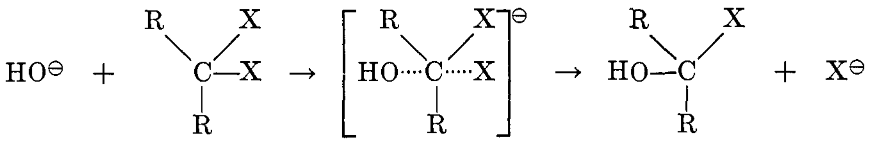
$$(C_6H_5)_3C^{\oplus} + H_2O \xrightarrow{\text{fast}} (C_6H_5)_3COH_2{}^{\oplus}$$

and it is probable that the remaining members of the carbon series hydrolyze by the same process (89). In the analogous silicon series, however, the hydrolysis proceeds by the S_N2 attack by a water molecule on the chlorosilane molecule (189). Swain, Esteve, and Jones have proposed that the first step in the hydrolysis involves the reversible formation of a pentacovalent intermediate, which then decomposes into the product in the second and rate-controlling step (189).



In view of the ability of silicon to expand its valence shell to accommodate more than eight electrons this is an attractive possibility. The evidence is inconclusive, however, and the reaction may well occur by "a modified S_N2 mechanism in which bond-making influences are dominant" (90). On either interpretation of the chlorosilane hydrolysis the contrast with the analogous carbon reaction is marked. In the carbon series 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 coördination step.

A further difference is noted in the alkyl series. Alkylhalosilanes 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 arylhalomethanes, and they do not all hydrolyze by the same mechanism. The tertiary alkyl halides hydrolyze by the same S_N1 mechanism outlined for the arylhalomethanes (7). The alkyldihalo- and alkyltrihalomethanes, 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 the S_N2 type. This S_N2 mechanism, however, would differ from the S_N2 mechanism which Swain proposed for the 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, chloro(triisopropyl)methane hydrolyzes six times more rapidly than *tert*-butyl chloride (8). In the silicon series the reverse is true. While chloro(trimethyl)silane hydrolyzes even in moist air, chloro(triisopropyl)silane is resistant to hydrolysis by ordinary means (64). 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 (27). In the silicon series internal strains are smaller, owing 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 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 (41, 98). 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 (147, 160) and probably proceeds by a similar mechanism. In the carbon series the reverse order probably holds, as in the case of hydrolysis (98). In ethanol the phenylsilicon 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 (124, 187, 188). The compound $C_6H_5C(OR)_3$ is produced only by the use of sodium alkoxide (124).

The relative rates of ammonolysis of halosilanes and halomethanes are probably similar to those of hydrolysis and alcoholysis. Thus, while alkyl 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 (32). The conditions are sufficiently mild so that the silicon analogs of primary and secondary amines can be prepared at will (119, 162), 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, $(SiH_3)_3N$. Trimethylchlorosilane and higher homologs will react with only two hydrogens of ammonia to give hexaalkyl analogs of secondary amines, such as hexamethyldisilazane, $(CH_3)_3SiNHSi(CH_3)_3$ (22).

The reduction of silicon halides to silicon hydrides has been reported only with lithium aluminum hydride (47). It takes place rapidly and almost quantitatively in ether. The reduction of alkyl halides by the same reagents also occurs, but less readily (97). 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 recorded, 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 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) is 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 (52, 53). In the carbon series, dimethylzinc with either *tert*-butyl iodide or 2,2-dichloropropane gives tetramethylmethane (127), but diethylzinc with chloroform and carbon tetrachloride gives ethylene and propylene (152). Pape introduced the use of the modified Wurtz reaction into organosilicon synthesis (145). The reaction is highly exothermic and leads conveniently only to tetrasubstituted silanes.

$$SiCl_4 + 4RCl + 8Na \rightarrow SiR_4 + 8NaCl$$

Reactions involving sodium and carbon tetrachloride or chloroform are explosive and do not yield any useful products (180, 181). Kipping (109) and Dilthey (38) introduced the use of the Grignard reagent for reactions with silicon tetrachloride and other chlorosilanes, and, until 1945 (156), 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 undoubtedly safe to say that more 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 (17), and with phenylmagnesium bromide gives triphenylmethyl peroxide, triphenylcarbinol, and hexaphenylethane (82).

The use of the equally convenient and more reactive organolithium reagents was introduced by Fleming (48) and by Gilman and Clark (63). These 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 (133) and by Wittig (204). In general, carbon tetrahalides and haloforms react with organolithium reagents 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–metal 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–metal 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 (44), as was mentioned under those headings. However, for preparing organosilicon compounds from silicon tetrachloride, aluminum chloride has some limited use. A method has been reported (172) for achieving the reaction of silicon tetrachloride with olefins in the presence of aluminum chloride at high temperatures and pressures to give trichloro(2-chloroalkyl)-silanes.

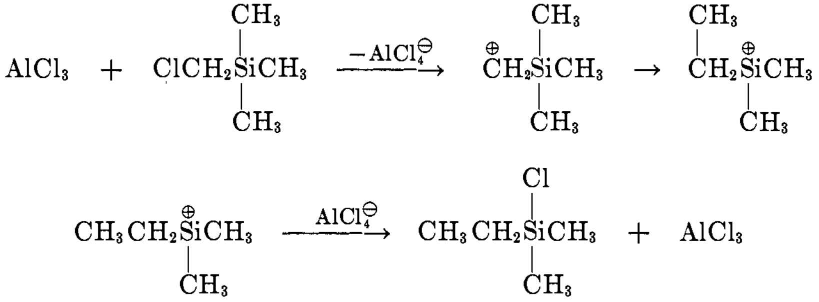
$$\mathrm{CH_2{=}CH_2 + SiCl_4 \rightarrow ClCH_2CH_2SiCl_3}$$

Saturated hydrocarbons are reported to react in the same way (137), as are alkyl halides (94). In the latter reaction the catalyst is aluminum metal; however, it is suggested 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 (194).

$$\mathrm{RCH{=}CH_2 + CH_3COX \xrightarrow{AlX_3} RCH{=}CHCOCH_3 + HX + RCHXCH_2COCH_3}$$

Reactions between alkyl chlorides and alkanes lead to isomerization, cracking, and polymerization rather than the desired coupling (194).

Whitmore has shown that aluminum chloride catalyzes the rearrangement of (chloromethyl)trimethylsilane to chloroethyldimethylsilane, and proposed a mechanism analogous to that encountered in similar rearrangements of hydrocarbon halides catalyzed by milder reagents (203).



$$\mathrm{AlCl_3} + \mathrm{ClCH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_3} \xrightarrow{-\mathrm{AlCl_4^{\ominus}}} \overset{\oplus}{\mathrm{C}}\mathrm{H_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_3} \rightarrow \overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{H_2}\overset{\oplus}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_3}$$

$$\mathrm{CH_3CH_2}\overset{\oplus}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_3} \xrightarrow{\mathrm{AlCl_4^{\ominus}}} \mathrm{CH_3CH_2}\overset{\mathrm{Cl}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CH_3} + \mathrm{AlCl_3}$$

The following redistribution reaction has also been found to be brought about by anhydrous aluminum chloride (203).

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

Finally, we may consider reactions of the halosilanes with active metals. The ordinary reaction in the silicon series is coupling to form disilanes, as was discussed under silicon–silicon bonds. In the carbon series heavy metals like silver and mercury cause coupling of triarylhalomethanes to hexaarylethanes, but alkali metals form triarylmethyl metallic compounds (3). The formation of silicon–metal bonds by this reaction has also been reported, but there is some doubt as to the correct interpretation of the experimental evidence. Kraus and Eatough (117) reported the preparation of triphenylsilyllithium by the reaction of bromotriphenylsilane with lithium in ethylamine. The reaction was unsuccessful with chlorotriphenylsilane because of solvolysis.

$$\mathrm{Li} + (\mathrm{C_6H_5})_3\mathrm{SiCl} + \mathrm{H_2NC_2H_5} \rightarrow (\mathrm{C_6H_5})_3\mathrm{SiNHC_2H_5} + \mathrm{LiCl} + \tfrac{1}{2}\mathrm{H_2}$$

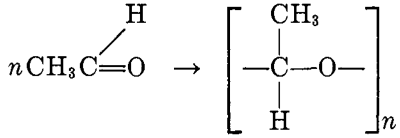
$$\mathrm{Li} + (\mathrm{C_6H_5})_3\mathrm{SiBr} + \mathrm{H_2NC_2H_5} \rightarrow (\mathrm{C_6H_5})_3\mathrm{Si}\cdot\mathrm{C_2H_5NH_2} + \mathrm{LiBr}$$

$$\mathrm{Li} + (\mathrm{C_6H_5})_3\mathrm{Si}\cdot\mathrm{C_2H_5NH_2} \rightarrow (\mathrm{C_6H_5})_3\mathrm{SiLi} + \mathrm{C_2H_5NH_2}$$

This point alone 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 attempts to repeat them have not been successful (11). The preparation of triphenylsilylpotassium from chlorotriphenylsilane and sodium–potassium alloy in ether has also been reported (76). However, since chlorotriphenylsilane and lithium or sodium are known to form hexaphenyldisilane (164, 67), and hexaphenyldisilane with sodium–potassium alloy is known to give triphenylsilylpotassium (76), all under the same conditions, it seems likely that the primary reaction of the chlorosilane is coupling in this case also.

G. 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-repellent properties. Strictly analogous carbon polyethers are unknown. These would be the result of ketone polymerization, but this has not been observed (15). Aldehydes give high polymers which are analogous to the polysiloxanes except that they contain an unsubstituted hydrogen atom in the chain (15).



$$n\,\mathrm{CH_3C(H){=}O} \rightarrow \left[\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{-C-O-}\\ |\\ \mathrm{H}\end{array}\right]_n$$

However, these compounds depolymerize so readily that they have had no industrial importance and consequently have not been studied extensively. 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 number of different reactions of prime theoretical and industrial importance. Organic compounds containing silicon–oxygen double bonds are unknown, probably for the reasons discussed under silicon–carbon double bonds.

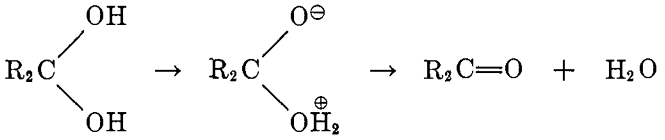
The physical constants available for silicon–oxygen and carbon–oxygen bonds are reported in table 1. It will be noted that the silicon–oxygen bond distance, like the silicon–fluorine bond distance, is less than the calculated value. This subject has been discussed under silicon–halogen bonds, and the 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.

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

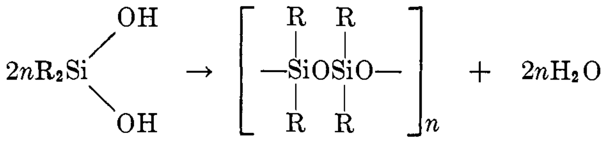
The reaction is catalyzed by both acids (73, 106) and bases (10, 69), and occurs so readily with alkyl- (159) and mixed alkylarylsilanols (72, 132) that the uncondensed silanols are frequently difficult to prepare. The corresponding preparation of ethers from alcohols is a much more difficult process, 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 series.

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:



$$R_2C(OH)_2 \rightarrow R_2C(O^{\ominus})(\overset{\oplus}{O}H_2) \rightarrow R_2C{=}O + H_2O$$

the last step being favored by the resonance energy of the carbonyl groups. This may explain why hemiacetals and acetals are increasingly more stable than *gem*-diols (141). In the silicon series, silicon–oxygen double bonds are not formed, so the dehydration must be intermolecular. Infrared studies of the polymeric products of such dehydrations as



$$2nR_2Si(OH)_2 \rightarrow \left[-\overset{R}{\underset{R}{Si}}O\overset{R}{\underset{R}{Si}}O- \right]_n + 2nH_2O$$

have shown no evidence for the presence of even small amounts of compounds containing silicon–oxygen double bonds.

Silanetriols have not been isolated as such, but probably form unstable intermediates in the hydrolysis of such compounds as trichlorophenylsilane to cross-linked polymers. In the carbon series some 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°C. (178). In view of the electropositive nature of silicon, this is surprising. It may be considered evidence for the participation of resonance structures such as $R_3SiOH \leftrightarrow R_3\overset{\ominus}{Si}{=}O\ \overset{\oplus}{H}$, with some reservations in view of the present dubious status of structures involving double bonds to silicon.

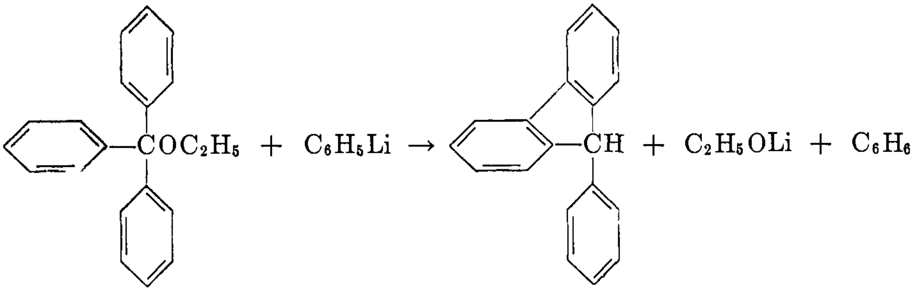
In accord with their considerable acidity, silanols react with alcohols to give compounds which resemble esters more than ethers. These compounds may be considered to be esters of orthosilicic acid and, in a general way, resemble the orthocarbonates or acetals. They are hydrolyzed to silanols and alcohols 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 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 (121). 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 (177), bases (106), and Grignard reagents (112, 159) to give silanols.

Alkoxytriphenylsilanes resemble alkoxytriphenylmethanes in one respect, at least; they react with alkali metals to give triphenylsilyl metallic (12) and triphenylmethyl metallic compounds (3), respectively. However, in a related reaction they differ, since ethoxytriphenylsilane and phenyllithium give tetraphenylsilane (77),

$$(C_6H_5)_3SiOC_2H_5 + C_6H_5Li \rightarrow (C_6H_5)_4Si + C_2H_5OLi$$

while ethoxytriphenylmethane and phenyllithium give 9-phenylfluorene (135).



The difference in the latter case is probably to be attributed, at least in part, to the greater steric crowding of phenyl groups around the central atom in the carbon compound.

The silanols behave like alcohols in their reactions with acids. Thus, anhydrous hydrogen chloride in ether converts most silanols to chlorosilanes (73, 120), some of the lower alkyl silanols being converted even by concentrated aqueous hydrochloric acid (178). Silyl esters of carboxylic acids are also known, but they are much more easily hydrolyzed than are ordinary alcoholic esters (169).

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 (177). 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 for tertiary aliphatic alcohols. In tertiary alcohols ionization takes place as follows:

$$ROH + H_2SO_4 \rightleftharpoons \overset{\oplus}{R}OH_2 + HSO_4^{\ominus} \quad (i = 2)$$

while in primary alcohols a further step involving a rearward attack by the bisulfate ion leads to

$$HSO_4^{\ominus} + \overset{\oplus}{R}OH_2 \rightleftharpoons RHSO_4 + H_2O$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3\overset{\oplus}{O} + HSO_4^{\ominus}$$

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 rearward attack is reduced in these compounds by the large size of the silicon atom (143).

H. 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 the hydrolysis are the relatively mild amines instead of the strongly corrosive halogen acids (23). 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 (162), or sodium in liquid ammonia (120). Silyl hydrides and metal amides also give aminosilanes in excellent yields (69, 119). Only two silyl groups can be attached to nitrogen except in the case of trisilylamine, $(SiH_3)_3N$ (22). Tri-*tert*-alkylamines are also unknown (135). 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 preparing halosilanes (4).

$$R_3SiNH_2 + HX \rightarrow R_3SiX + NH_3$$

None of 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 hydrogen–nitrogen bond. Carboxylic acids, for example, give ammonia and silyl esters of the acids (140).

Burg and Kuljian have found that trisilylamine, $(SiH_3)_3N$, is a much weaker electron donor in reactions with trihalo- and trimethylboron than is trimethylamine, $(CH_3)_3N$ (28). 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

$$(SiH_3)_3N\colon \leftrightarrow H_3\overset{\ominus}{Si}{=}\overset{\oplus}{N}(SiH_3)_2$$

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 hydrolyzed in aqueous solvents (2), and, also like the halosilanes, the ease of hydrolysis increases as the number of isocyanate groups on the silicon atom increases (1). One such compound, triphenylsilyl isothiocyanate, also behaved like a halosilane toward phenyllithium, giving tetraphenylsilane (68). Organic isocyanates react with Grignard and organolithium reagents to give substituted amides (70), and the products from the reaction of triphenylsilyl isothiocyanate with Grignard reagents, and of triphenylsilyl isocyanate with both Grignard and organolithium reagents, can be looked upon as the hydrolysis products of the corresponding *N*-silylamide (68).

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

$$(C_6H_5)_3SiN{=}C(C_6H_5)OLi \xrightarrow{H_2O} (C_6H_5)_3SiN{=}C(C_6H_5)OH \rightarrow (C_6H_5)_3SiNHCOC_6H_5$$

$$(C_6H_5)_3SiNHCOC_6H_5 + H_2O \rightarrow (C_6H_5)_3SiOH + C_6H_5CONH_2$$

In general, however, the silyl isocyanates and isothiocyanates do not react like their carbon analogs. As has been emphasized, they hydrolyze more easily than alkyl isocyanates, 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 urethans or with amines to give ureas. Rather, the reverse happens. Triphenylsilyl isocyanate and triphenylsilyl isothiocyanate are conveniently prepared by the reaction of chlorotriphenylsilane with urea, thiourea, or sodium urethan, as the case may be (2).

I. 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 aryloxysilanes 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 thiophenoxytriphenylsilane 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 (75).

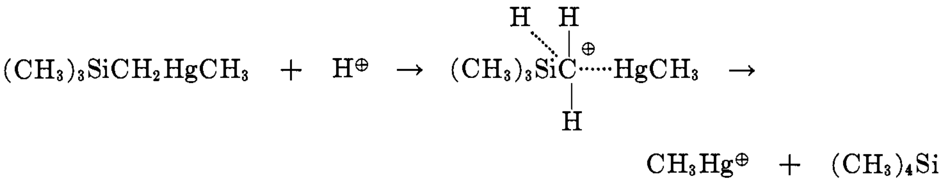
Kraus has reported the preparation of triphenylsilyltrimethyltin (117) and triethylsilyltriphenylgermanium (119). Not much is known about the properties of these compounds, but they seem to resemble the ditin and digermanium compounds, since they are cleaved by halogens and by sodium in liquid ethylamine.

J. Effect of silicon on adjacent bonds

A large proportion of the work on the "silicon effect," as well as the term itself, is due to Whitmore and coworkers. They first prepared chloromethyltrimethylsilane, $(CH_3)_3SiCH_2Cl$, and found the halogen to be much more reactive than the corresponding halogen of neopentyl chloride, $(CH_3)_3CCH_2Cl$, toward nucleophilic reagents. They attributed the unreactivity of the neopentyl chloride to the steric shielding of the methylene carbon to rearward attack, and the lability of the halogen in the silicon analog to diminished shielding by the groups attached to the larger silicon atom (202). 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 that 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.



$$(CH_3)_3SiCH_2HgCH_3 + H^{\oplus} \rightarrow (CH_3)_3Si\underset{H}{\overset{H\ \ H\ \oplus}{C}}\cdots HgCH_3 \rightarrow CH_3Hg^{\oplus} + (CH_3)_4Si$$

This interpretation can be shown to account satisfactorily for the series of relative "electronegativities" obtained from the cleavage 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.

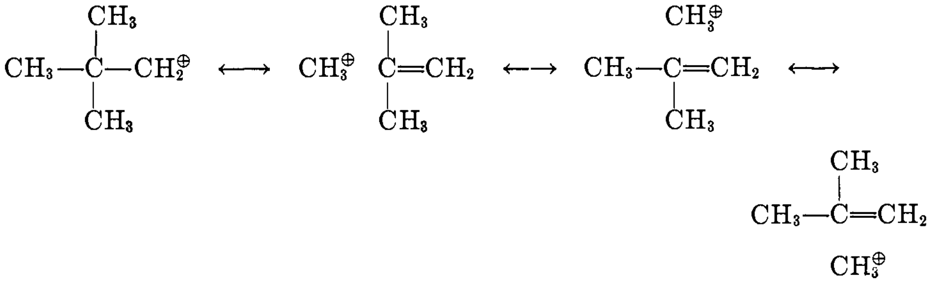
It will be noted that these reactions imply a greater basicity for a carbon atom attached to the trimethylsilyl group than for one attached to the *tert*-butyl group. This is exactly the opposite to the situation with oxygen and nitrogen attached to silicon. Oxygen and nitrogen both have unshared electron pairs which can be used to form resonance structures having double bonds to silicon, such as $R_3\overset{\ominus}{Si}{=}\overset{\oplus}{O}H$ and $R_3\overset{\ominus}{Si}{=}\overset{\oplus}{N}H_2$, 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 $R_3\overset{\oplus}{Si}\overset{\ominus}{C}H_2R$.

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

The unreactivity of (chloromethyl)trimethylsilane may be illustrated in terms of the mechanism below:

$$(CH_3)_3SiCH_2Cl \quad + \quad Ag^{\oplus} \quad \xrightarrow{-AgCl} \quad (CH_3)_3SiCH^{\oplus} \quad \xrightarrow{H_2O} \quad (CH_3)_3SiCH_2\overset{\oplus}{O}H_2$$

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 cations can be stabilized by resonance contributions from hyperconjugative structures such as

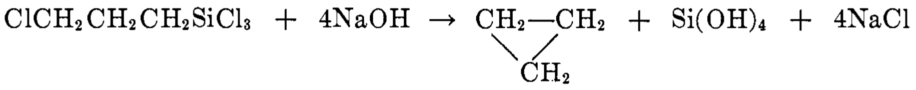


$$CH_3{—}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{—}CH_2^{\oplus} \longleftrightarrow CH_3^{\oplus}\ \underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{=}CH_2 \longleftrightarrow CH_3{—}\underset{CH_3}{\overset{CH_3^{\oplus}}{\underset{|}{C}}}{=}CH_2 \longleftrightarrow CH_3{—}\underset{CH_3^{\oplus}}{\overset{CH_3}{\overset{|}{C}}}{=}CH_2$$

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 coworkers next prepared the 2-chloro- and 3-chloroalkyltrichlorosilanes. The carbon–chlorine bonds in both of these compounds were more reactive towards nucleophilic reagents than in the chloromethylsilanes, the 2-chloro- compounds being more reactive than the 3-chloro- ones. With aqueous bases these compounds reacted as follows (175):

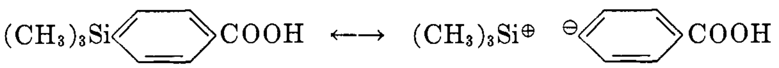
$$ClCH_2CH_2SiCl_3 + 4NaOH \rightarrow CH_2{=}CH_2 + Si(OH)_4 + 4NaCl$$



Such reactions with the analogous carbon compounds are unknown. The difference was interpreted in terms of the greater ease of attack by nucleophilic reagents on a silicon than on a carbon atom (174). Oxygen on an alkyl carbon atom beta to silicon produced a similar lability of the silicon–carbon bond (81).

Somewhat later, the same group of workers (176) determined the dissociation constants of a number of substituted acetic acids, RCH_2COOH, obtaining decreasing acidities as R was changed in the order $(CH_3)_3C > (CH_3)_3SiCH_2 > (CH_3)_3Si > C_6H_5(CH_3)_2Si$. Again the effects were attributed to the electron-releasing properties of the silicon atom as compared to carbon.

A similar effect was noted by Roberts and coworkers in a less ambiguous situation (153). They determined the sigma 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 be more acid-weakening than the *tert*-butyl group, and attributed this to an inductive effect of electron release in the silicon–carbon bond, such as



which is evidently greater than in the carbon analog.

IV. PHYSIOLOGICAL PROPERTIES

In general, the organosilicon compounds seem to be less active physiologically than their carbon analogs. 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 ethylsilanes. The ethoxysilanes are less toxic, the minimum lethal dose in rats being 5–10 g./kg. for the various methyl- and ethylethoxysilanes (157). However, apart from this result of their ease of hydrolysis, the organosilicon compounds seem to be rather inert physiologically, at least in the few cases which have received study.

For example, rats were unaffected when exposed to air containing 25,000 p.p.m. of hexamethyldisiloxane for periods of 30 min., and hexamethyldisiloxane and many other polysiloxanes showed no skin or eye irritation and had no harmful effect on peritoneal injection (157). Since these compounds are extremely insoluble in water, as are the tetrasubstituted silanes, any physiological activity which 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.

Some attention has been devoted to the preparation of silicon analogs of physiologically active carbon compounds (59). The results of physiological tests on most of these compounds are not yet known, however. A silicon near-analog of DDT (138) seemed to have negligible insecticidal properties in preliminary tests.

Since the physicochemical 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 silicon analogs of active carbon compounds might be a promising approach. The silicon compounds would be distorted in shape, as well as larger in size, when compared with their carbon analogs. It is possible that this ability to alter the shape and size of molecules without greatly altering their fundamental structure could be useful in elucidating the processes involved in physiological activity.

V. REFERENCES

(1) ANDERSON, H. H.: J. Am. Chem. Soc. **70**, 1220 (1948).

(2) ANDERSON, H. H.: J. Am. Chem. Soc. **72**, 193 (1950).

(3) BACHMANN, W. E.: In *Organic Chemistry, an Advanced Treatise*, edited by H. Gilman, 2nd edition, Vol. 1, Chapter 6. John Wiley and Sons, Inc., New York (1943).

(4) BAILEY, D. L., SOMMER, L. H., AND WHITMORE, F. C.: J. Am. Chem. Soc. **70**, 435 (1948).

(5) BARRY, A. J.: J. Applied Phys. **17**, 1020 (1946).

(6) BARRY, A. J., DEPREE, L., GILKEY, J. W., AND HOOK, D. E.: J. Am. Chem. Soc. **69**, 2916 (1947).

(7) BARTLETT, P. D.: J. Am. Chem. Soc. **61**, 1630 (1939).

(8) BARTLETT, P. D.: Abstracts of Papers, Tenth National Organic Chemistry Symposium, Boston, Massachusetts, 1947.

(9) BARTLETT, P. D., CONDON, F. E., AND SNYDER, A.: J. Am. Chem. Soc. **66**, 1531 (1944).

(10) BASSETT, E. A., EMBLEM, H. G., FRANKEL, M., AND RIDGE, D.: J. Soc. Chem. Ind. **67**, 177 (1948).

(11) BENKESER, R. A. (Purdue University): Private communication.
BENKESER, R. A., ROBINSON, R. E., AND LANDESMAN, H.: Abstracts of Papers Presented before the Division of Organic Chemistry of the American Chemical Society, Atlantic City, New Jersey, September 14–19, 1952, p. 44M.

(12) BENKESER, R. A., LANDESMAN, H., AND FOSTER, D. J.: J. Am. Chem. Soc. **74**, 648 (1952).

(13) BENKESER, R. A., AND SEVERSON, R. G.: J. Am. Chem. Soc. **73**, 1424 (1951).

(14) BERTHELOT, M.: Ann. **109**, 121 (1859).

(15) BEVINGTON, J. C.: Quart. Revs. (London) **6**, 141 (1952).

(16) Bichowski, F. R., and Rossini, F. D.: *The Thermochemistry of the Chemical Substances.* Reinhold Publishing Corporation, New York (1936).
(17) Binaghi, R.: Gazz. chim. ital. **53,** 886 (1923).
(18) Booth, H. S., and Jarry, R. L.: J. Am. Chem. Soc. **71,** 971 (1949).
(19) Booth, H. S., and Stillwell, W. D.: J. Am. Chem. Soc. **56,** 1531 (1934).
(20) Booth, H. S., and Swinehart, C. F.: J. Am. Chem. Soc. **54,** 4750 (1932).
(21) Booth, H. S., and Swinehart, C. F.: J. Am. Chem. Soc. **57,** 1333 (1935).
(22) Brewer, S. D., and Haber, C. P.: J. Am. Chem. Soc. **70,** 3886 (1948).
(23) British Thomson-Houston Co., Ltd: British patent 599,153 (1948).
(24) Brockway, L. O., and Davidson, N. R.: J. Am. Chem. Soc. **63,** 3287 (1941).
(25) Brockway, L. O., and Jenkins, H. O.: J. Am. Chem. Soc. **58,** 2036 (1936).
(26) Brockway, L. O., and Jenkins, H. O.: J. Am. Chem. Soc. **68,** 719 (1946).
(27) Brown, H. C.: Science **103,** 2674 (1946).
(28) Burg, A. B., and Kuljian, E. S.: J. Am. Chem. Soc. **72,** 3103 (1950).
(29) Burkhard, C. A.: J. Am. Chem. Soc. **71,** 963 (1949).
(30) Burkhard, C. A., and Krieble, R. H.: J. Am. Chem. Soc. **69,** 2887 (1947).
(31) Burkhard, C. A., and Norton, F. J.: Anal. Chem. **21,** 304 (1949).
(32) Burkhard, C. A., Rochow, E. G., Booth, H. S., and Hartt, J.: Chem. Revs. **41,** 97 (1947).
(33) Curran, C., Witucki, R. M., and McCusker, P. A.: J. Am. Chem. Soc. **72,** 4471 (1950).
(34) Dailey, B. R., Mays, J. M., and Towne, C. H.: Phys. Rev. **76,** 136 (1949).
(35) Denbigh, K. G.: Trans. Faraday Soc. **36,** 936 (1946).
(36) Dewar, M. J. S.: *The Electronic Theory of Organic Chemistry.* Oxford University Press, London (1949).
(37) Digiorgio, P. A., Sommer, L. H., and Whitmore, F. C.: J. Am. Chem. Soc. **70,** 3512 (1948).
(38) Dilthey, W., and Eduardoff, F.: Ber. **37,** 1139 (1904).
(39) Doescher, Q. N.: J. Chem. Phys. **19,** 1070 (1951).
(40) Dolgov, B. N., and Panina, O. K.: Zhur. Obshcheĭ Khim. **18,** 1293 (1948); Chem. Abstracts **43,** 2177 (1949).
(41) Eaborn, C.: J. Chem. Soc. **1950,** 3077.
(42) Emeléus, H. J., and Payne, D. S.: J. Chem. Soc. **1947,** 1590.
(43) Emeléus, H. J., and Robinson, S. R.: J. Chem. Soc. **1947,** 1592.
(44) Evison, W. E., and Kipping, F. S.: J. Chem. Soc. **1931,** 2774.
(45) Fajans, K.: Z. Physik **1,** 101 (1920).
(46) Field, F. H.: J. Chem. Phys. **19,** 793 (1951).
(47) Finholt, A. E., Bond, A. C., Wilzbach, K. E., and Schlesinger, H. I.: J. Am. Chem. Soc. **69,** 2692 (1947).
(48) Fleming, R.: U. S. patent 2,386,452; Chem. Abstracts **40,** 603 (1946).
(49) Forbes, G. S., and Anderson, H. H.: J. Am. Chem. Soc. **70,** 1043 (1948).
(50) Forbes, G. S., and Anderson, H. H.: J. Am. Chem. Soc. **70,** 1222 (1948).
(51) Fox, H. W., Taylor, P. W., and Zisman, W. A.: Ind. Eng. Chem. **39,** 1401 (1947).
(52) Friedel, C., and Crafts, J. M.: Ann. **127,** 28 (1863).
(53) Friedel, C., and Crafts, J. M.: Ann. **136,** 203 (1865).
(54) Friedel, C., and Ladenburg, A.: Ann. **145,** 179 (1868).
(55) Friedel, C., and Ladenburg, A.: Ann. **203,** 241 (1880).
(56) Friend, J. N.: *A Textbook of Inorganic Chemistry.* C. Griffin and Co., Ltd., London (1921).
(57) Gatterman, L.: Ber. **22,** 186 (1889).
(58) Gilliam, O. R., Edwards, D. H., and Gordy, W.: Phys. Rev. **75,** 1014 (1949).
(59) Gilman, H.: Unpublished studies.
(60) Gilman, H., Benkeser, R. A., and Dunn, G. E.: J. Am. Chem. Soc. **72,** 1689 (1950).
(61) Gilman, H., and Brannen, C. G.: J. Am. Chem. Soc. **73,** 4640 (1951).

(62) Gilman, H., Brown, G. E., Webb, F. J., and Spatz, S. M.: J. Am. Chem. Soc. **62**, 977 (1940).
(63) Gilman, H., and Clark, R. N.: J. Am. Chem. Soc. **68**, 1675 (1946).
(64) Gilman, H., and Clark, R. N.: J. Am. Chem. Soc. **69**, 1499 (1947).
(65) Gilman, H., and Dunn, G. E.: J. Am. Chem. Soc. **72**, 2178 (1950).
(66) Gilman, H., and Dunn, G. E.: J. Am. Chem. Soc. **73**, 3404 (1951).
(67) Gilman, H., and Dunn, G. E.: J. Am. Chem. Soc. **73**, 4499 (1951).
(68) Gilman, H., Hofferth, B., and Melvin, H. W.: J. Am. Chem. Soc. **72**, 3045 (1950).
(69) Gilman, H., Hofferth, B., Melvin, H. W., and Dunn, G. E.: J. Am. Chem. Soc. **72**, 5767 (1950).
(70) Gilman, H., Kirby, J. E., and Kinney, C. R.: J. Am. Chem. Soc. **51**, 2252 (1929).
(71) Gilman, H., and Marshall, F. J.: J. Am. Chem. Soc. **71**, 2066 (1949).
(72) Gilman, H., and Massie, S. P.: J. Am. Chem. Soc. **68**, 1128 (1946).
(73) Gilman, H., and Melvin, H. W.: Unpublished studies.
(74) Gilman, H., and Smart, G. N. R.: J. Org. Chem. **15**, 720 (1950).
(75) Gilman, H., and Smart, G. N. R.: J. Org. Chem. **16**, 424 (1951).
(76) Gilman, H., and Wu, T. C.: J. Am. Chem. Soc. **73**, 4031 (1951).
(77) Gilman, H., and Wu, T. C.: Unpublished studies.
(78) Gilman, H., Wu, T. C., Hartzfeld, H. A., Guter, G. A., Smith, A. G., Goodman, J. J., and Eidt, S. H.: J. Am. Chem. Soc. **74**, 561 (1952).
(79) Gilman, H., and Young, R. V.: J. Org. Chem. **1**, 315 (1936).
(80) Glockler, G.: J. Chem. Phys. **19**, 124 (1951).
(81) Gold, J. R., Sommer, L. H., and Whitmore, F. C.: J. Am. Chem. Soc. **70**, 2874 (1948).
(82) Gomberg, M., and Cone, L. H.: Ber. **39**, 1462, 1466 (1906).
(83) Gordy, W.: J. Chem. Phys. **15**, 81 (1947).
(84) Hagstrum, H. D.: Phys. Rev. **72**, 947 (1947).
(85) Hammett, L. P.: *Physical Organic Chemistry.* McGraw-Hill Book Company, Inc., New York (1940).
(86) Hanriot, M., and St. Pierre, O.: Bull. soc. chim. France [3] **1**, 774 (1890).
(87) Helm, D. F., and Mack, E.: J. Am. Chem. Soc. **59**, 60 (1937).
(88) Herzberg, G.: J. Chem. Phys. **10**, 306 (1942).
(89) Hine, J., and Lee, D. E.: J. Am. Chem. Soc. **73**, 22 (1951).
(90) Hughes, E. D.: Quart. Revs. (London) **5**, 245 (1951).
(91) Hughes, E. D., and Taher, N. A.: J. Chem. Soc. **1940**, 936.
(92) Hunter, M. J., Hyde, J. F., Warrick, E. L., and Fletcher, H. J.: J. Am. Chem. Soc. **68**, 667 (1946).
(93) Hunter, M. J., Warrick, E. L., Hyde, J. F., and Currie, C. C.: J. Am. Chem. Soc. **68**, 2284 (1946).
(94) Hurd, D. T.: J. Am. Chem. Soc. **67**, 1545 (1945).
(95) Ipatiev, W., and Dolgov, B.: Ber. **62**, 1220 (1929).
(96) Jenkins, J. W., and Post, H. W.: J. Org. Chem. **15**, 556 (1950).
(97) Johnson, J. E., Blizzard, R. H., and Carhart, H. W.: J. Am. Chem. Soc. **70**, 3664 (1948).
(98) Johnson, J. R.: In *Organic Chemistry, an Advanced Treatise*, edited by H. Gilman, 2nd edition, Vol. 2, Chapter 25. John Wiley and Sons, Inc., New York (1943).
(99) Jones, W. J., Thomas, L. H., Pritchard, E. H., and Bowden, S. T.: J. Chem. Soc. **1946**, 324.
(100) Kharasch, M. S., Jensen, E. V., and Urry, W. H.: J. Am. Chem. Soc. **69**, 1100 (1947).
(101) Kinney, C. R.: J. Am. Chem. Soc. **60**, 3032 (1938).
(102) Kinney, C. R.: Ind. Eng. Chem. **32**, 559 (1940).
(103) Kinney, C. R.: Ind. Eng. Chem. **33**, 791 (1941).
(104) Kinney, C. R.: J. Org. Chem. **6**, 220, 224 (1941).
(105) Kinney, C. R.: J. Org. Chem. **7**, 111 (1942).

(106) Kipping, F. S.: J. Chem. Soc. **79,** 449 (1901).
(107) Kipping, F. S.: J. Chem. Soc. **119,** 647 (1921).
(108) Kipping, F. S.: J. Chem. Soc. **1927,** 104.
(109) Kipping, F. S.: Proc. Chem. Soc. (London) **20,** 15 (1904).
(110) Kipping, F. S.: Proc. Chem. Soc. (London) **27,** 143 (1911).
(111) Kipping, F. S.: Proc. Roy. Soc. (London) **159A,** 139 (1937).
(112) Kipping, F. S., and Hackford, J. E.: J. Chem. Soc. **99,** 138 (1911).
(113) Kipping, F. S., and Murray, A. G.: J. Chem. Soc. **1929,** 360.
(114) Kipping, F. S., Murray, A. G., and Maltby, J. G.: J. Chem. Soc. **1929,** 1108.
(115) Kipping, F. S. and Sands, J. E.: J. Chem. Soc. **119,** 330 (1921).
(116) Kipping, F. S., and Sands, J. E.: J. Chem. Soc. **119,** 849 (1921).
(117) Kraus, C. A., and Eatough, H.: J. Am. Chem. Soc. **55,** 5008 (1933).
(118) Kraus, C. A., and Greer, W. N.: J. Am. Chem. Soc. **44,** 2629 (1922).
(119) Kraus, C. A., and Nelson, W. K.: J. Am. Chem. Soc. **56,** 197 (1934).
(120) Kraus, C. A., and Rosen, R.: J. Am. Chem. Soc. **47,** 2739 (1925).
(121) Krieble, R. H., and Burkhard, C. A.: J. Am. Chem. Soc. **69,** 2689 (1947).
(122) Krieble, R. H., and Elliott, J. R.: J. Am. Chem. Soc. **68,** 2291 (1946).
(123) Lewis, R. N., and Newkirk, A. B.: J. Am. Chem. Soc. **69,** 701 (1947).
(124) Limpricht, H.: Ann. **135,** 80 (1865).
(125) Livingston, R. L., and Brockway, L. O.: J. Am. Chem. Soc. **66,** 94 (1944).
(126) Long, L. H., and Norrish, R. W. G.: Proc. Roy. Soc. (London) **187A,** 337 (1946).
(127) Lwow, M.: Z. Chem. **1870,** 520; *Beilstein's Handbuch der organischen Chemie,* 4th edition, Vol. 4, p. 672, Julius Springer, Berlin (1922).
(128) Machatschki, F.: Z. Krist. **94,** 222 (1936).
(129) Mackenzie, C. A., Mills, A. P., and Scott, J. M.: J. Am. Chem. Soc. **72,** 2032 (1950).
(130) Maddock, A. G., Reid, C., and Emeléus, H. J.: Nature **144,** 328 (1939).
(131) Manulkin, Z. M.: Zhur. Obshcheĭ Khim. **18,** 299 (1948); Chem. Abstracts **42,** 6742 (1948).
(132) Marsden, H., and Kipping, F. S.: J. Chem. Soc. **93,** 198 (1908).
(133) Marvel, C. S., Hager, F. D., and Coffman, D. D.: J. Am. Chem. Soc. **49,** 2323 (1927).
(134) Meals, R. N.: J. Am. Chem. Soc. **68,** 1880 (1948).
(135) Meikle, W. J. (Iowa State College): Private communication.
(136) Mellor, J. W.: *Comprehensive Treatise on Inorganic and Theoretical Chemistry.* Longmans, Green and Company, London (1946).
(137) Miller, H. C., and Schreiber, R. S.: U. S. patent 2,379,821 (1945).
(138) Miller, L. S.: Doctoral Dissertation, Iowa State College, 1950.
(139) Milligan, J. G., and Krause, C. A.: J. Am. Chem. Soc. **72,** 5300 (1950).
(140) Miner, C. S., Bryan, L. A., Holysz, R. P., and Pedlow, G. W.: Ind. Eng. Chem. **39,** 1368 (1947).
(141) Morton, J. W. (Iowa State College): Private communication.
(142) Mulliken, R. S.: J. Am. Chem. Soc. **72,** 4493 (1950).
(143) Newman, M. S., Craig, R. A., and Garrett, A. V.: J. Am. Chem. Soc. **71,** 869 (1949).
(144) Nomenclature, Spelling, and Pronunciation Committee of the American Chemical Society: Chem. Eng. News **24,** 1233 (1946).
(145) Pape, C.: Ann. **222,** 254 (1884).
(146) Pauling, L.: *The Nature of the Chemical Bond,* 2nd edition. Cornell University Press, Ithaca, New York (1940).
(147) Peppard, D., Brown, W., and Johnson, W.: J. Am. Chem. Soc. **68,** 70 (1946).
(148) Pitzer, K. S.: J. Am. Chem. Soc. **70,** 2140 (1948).
(149) Post, H. W.: *Silicones and Other Organic Silicon Compounds.* Reinhold Publishing Corporation, New York (1949).
(150) Pray, B. C., Sommer, L. H., Goldberg, G. H., Kerr, G. T., Digiorgio, P. A., and Whitmore, F. C.: J. Am. Chem. Soc. **70,** 433 (1948).

(151) Price, F. P.: J. Am. Chem. Soc. **69**, 2600 (1947).

(152) Reith, R., and Beilstein, F.: Ann. **124**, 242, 245 (1862).

(153) Roberts, J. D., McElhill, E. A., and Armstrong, R.: J. Am. Chem. Soc. **71**, 2923 (1949).

(154) Rochow, E. G.: *An Introduction to the Chemistry of the Silicones*, 1st edition, p. 45. John Wiley and Sons, Inc., New York (1946).

(155) Rochow, E. G.: *An Introduction to the Chemistry of the Silicones*, 2nd edition. John Wiley and Sons, Inc., New York (1951).

(156) Rochow, E. G.: J. Am. Chem. Soc. **67**, 963 (1945).

(157) Rowe, V. K., Spencer, H. C., and Bass, S. L.: J. Ind. Hyg. Toxicol. **30**, 332 (1948).

(158) Ruff, O., and Albert, C.: Ber. **38**, 53, 2222 (1905).

(159) Sauer, R. O.: J. Am. Chem. Soc. **66**, 1707 (1944).

(160) Sauer, R. O.: J. Am. Chem. Soc. **68**, 138 (1946).

(161) Sauer, R. O.: J. Am. Chem. Soc. **68**, 954 (1946).

(162) Sauer, R. O., and Hasek, R. H.: J. Am. Chem. Soc. **68**, 241 (1946).

(163) Schlenk, W.: Ann. **394**, 221 (1912).

(164) Schlenk, W., Renning, J., and Racky, G.: Ber. **44**, 1178 (1911).

(165) Schomaker, V., and Stevenson, D. P.: J. Am. Chem. Soc. **63**, 37 (1941).

(166) Schumb, W.: Inorg. Syntheses **1**, 38 (1939).

(167) Schumb, W., and Gamble, E.: Inorg. Syntheses **1**, 42 (1939).

(168) Schumb, W. C., and Saffer, C. M.: J. Am. Chem. Soc. **61**, 363 (1939).

(169) Schuyten, H. A., Weaver, J. W., and Reid, J. D.: J. Am. Chem. Soc. **69**, 2110 (1947).

(170) Schwartz, R., and Danders, C.: Chem. Ber. **80**, 444 (1947).

(171) Schwartz, R., and Meckbach, H.: Z. anorg. allgem. Chem. **232**, 241 (1937).

(172) Shtetter, I. I.: Russian patent 44,934 (1935); Chem. Abstracts **32**, 2958 (1938).

(173) Skinner, H. A.: Trans. Faraday Soc. **41**, 645 (1945).

(174) Sommer, L. H., Bailey, D. L., and Whitmore, F. C.: J. Am. Chem. Soc. **70**, 2869 (1948).

(175) Sommer, L. H., Dorfman, E., Goldberg, G. M., and Whitmore, F. C.: J. Am. Chem. Soc. **68**, 488 (1946).

(176) Sommer, L. H., Gold, J. R., Goldberg, G. N., and Marans, N. S.: J. Am. Chem. Soc. **71**, 1509 (1949).

(177) Sommer, L. H., Kerr, C. P., and Whitmore, F. C.: J. Am. Chem. Soc. **70**, 445 (1948).

(178) Sommer, L. H., Pietrusza, E. W., and Whitmore, F. C.: J. Am. Chem. Soc. **68**, 2282 (1946).

(179) Sommer, L. H., Pietrusza, E. W., and Whitmore, F. C.: J. Am. Chem. Soc. **69**, 188 (1947).

(180) Staudinger, H.: Z. angew. Chem. **35**, 659 (1922).

(181) Staudinger, H.: Z. angew. Chem. **38**, 578 (1925).

(182) Steacie, E. W. R.: *Atomic and Free Radical Reactions.* Reinhold Publishing Corporation, New York (1946).

(183) Stock, A., and Somieski, C.: Ber. **50**, 1378 (1917).

(184) Stock, A., and Somieski, C.: Ber. **51**, 989 (1918).

(185) Stock, A., and Somieski, C.: Ber. **52**, 695 (1919).

(186) Stokland, K.: Trans. Faraday Soc. **44**, 545 (1948).

(187) Straus, F., and Ecker, O.: Ber. **39**, 2977 (1906).

(188) Straus, F., and Hussy, W.: Ber. **42**, 2168 (1909).

(189) Swain, C. G., Esteve, R. M., and Jones, R. H.: J. Am. Chem. Soc. **71**, 965 (1949).

(190) Szwarc, M.: Chem. Revs. **47**, 75 (1950).

(191) Tanaka, T., Takahashi, U., Okawara, R., and Watase, T.: J. Chem. Phys. **19**, 1330 (1951).

(192) Tchitchibabine, Elgasine, S., and Lengold, V.: Bull. soc. chim. France [4] **43**, 238 (1928).

(193) Theilacker, W., and Ewald, M. L.: Naturwissenschaften **31**, 302 (1943).

(194) Thomas, C. A.: *Anhydrous Aluminum Chloride in Organic Chemistry.* Reinhold Publishing Corporation, New York (1941).
(195) Ullmann, F., and Munzhuber, A.: Ber. **36**, 404 (1903).
(196) Walsh, A. D.: J. Chem. Soc. **1948**, 398.
(197) Waring, C. E.: Trans. Faraday Soc. **36**, 1142 (1940).
(198) Warrick, E. L.: J. Am. Chem. Soc. **68**, 2455 (1946).
(199) Westheimer, F. H.: J. Am. Chem. Soc. **62**, 1892 (1940).
(200) Westheimer, F. H., and Metcalf, R. P.: J. Am. Chem. Soc. **63**, 1339 (1941).
(201) Whitmore, F. C., Pietrusza, E. W., and Sommer, L. H.: J. Am. Chem. Soc. **69**, 2108 (1947).
(202) Whitmore, F. C., Sommer, L. H., Digiorgio, P. A., Strong, W. A., van Strien, R. E., Bailey, D. L., Hall, H. K., Pietrusza, E. W., and Kerr, G. T.: J. Am. Chem. Soc. **68**, 475 (1946).
(203) Whitmore, F. C., Sommer, L. H., and Gold, J.: J. Am. Chem. Soc. **69**, 1976 (1947).
(204) Wittig, G., and Witt, H.: Ber. **74B**, 1474 (1941).
(205) Wöhler, F.: Ann. **127**, 257 (1863).
(206) Yakubovich, A. Y., and Ginsberg, V. A.: Uspekhi Khim. **18**, 46 (1949); Chem. Abstracts **44**, 1404 (1950).