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TRIS(TRIMETHYLSILYL)SILYLLITHIUM

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SUMMARY

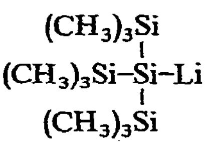
An investigation has been made of the relative reactivity of tris(trimethylsilyl)silyllithium (I) in an attempt to estimate the importance of (d_π-p_π) bonding involving two contiguous silicon atoms. The procedures used were: (1) a comparative metalation reaction; (2) a kinetic study; and (3) a cleavage reaction of a silicon–silicon bond. The results are not definitive, although they seem to imply that the reactivity of I is comparable to or less than that of triphenylsilyllithium.

The reactivity of I, together with its ultraviolet and NMR spectra, has been explained in terms of dative π-bonding.

INTRODUCTION

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 the carbon analog. Thus, for many years, participation of the vacant 3*d* orbitals of the silicon atom has been invoked to explain differences in the chemical and physical properties of structurally analogous silicon and carbon compounds[1,2].

From a structural point of view, we had available a novel type of silyllithium compound; namely, tris(trimethylsilyl)silyllithium (I)[3,4]. The uncommon, symmetrical arrangement of three trimethylsilyl groups bonded to the silicon-bearing lithium atom, together with failures to prepare stable solutions of trimethylsilyllithium*, prompted a study to determine the importance of dative π-bonding between contiguous silicon atoms in such species.



$$\begin{array}{c} (CH_3)_3Si \\ | \\ (CH_3)_3Si{-}Si{-}Li \\ | \\ (CH_3)_3Si \end{array}$$

I

We now wish to report evidence for the simultaneous participation of two silicon atoms in dative (d_π–p_π) bonding with each other: one atom acting as an electron acceptor and the other as the electron donor.

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* The preparation and properties of organosilylmetallic compounds have been thoroughly reviewed[1,5,6]. See ref. 7 for recent preparations of triethylsilyllithium and trimethylsilyllithium.

RESULTS

Preparation of tris(trimethylsilyl)silyllithium (I) and its reaction with fluorene

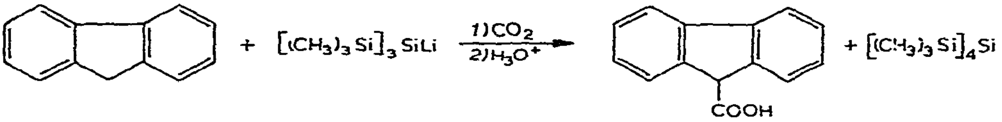
The reaction of tetrakis(trimethylsilyl)silane (II)[8,9] and methyllithium in tetrahydrofuran (THF)/ether (4/1) gave a pale greenish-yellow colored solution of tris(trimethylsilyl)silyllithium (I)[3,4]:

$$\underset{\text{II}}{[(CH_3)_3Si]_4Si} + CH_3Li \rightarrow \underset{\text{I}}{[(CH_3)_3Si]_3SiLi} + (CH_3)_4Si$$

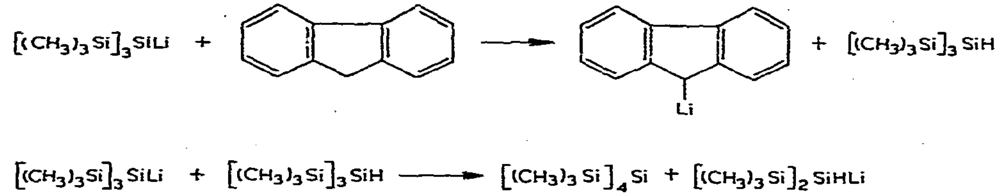
In this investigation, the volatile tetramethylsilane and ether were removed by distillation. The high purity of the resulting THF solution of the silyllithium compound was indicated by vapor phase chromatography of a hydrolyzed aliquot and the NMR spectrum of the silyllithium solution. Also, an 88% yield of tris(trimethylsilyl)silane was isolated subsequent to acid hydrolysis of tris(trimethylsilyl)silyllithium, indicating a high yield of the silyllithium compound[3,4]:

$$[(CH_3)_3Si]_3SiLi + H_3O^+ \rightarrow [(CH_3)_3Si]_3SiH$$

Treatment of tris(trimethylsilyl)silyllithium with fluorene at room temperature in THF afforded, subsequent to carbonation and acid hydrolysis, tetrakis(trimethylsilyl)silane, 9-fluorenecarboxylic acid and polymeric material:



The high yield of tetrakis(trimethylsilyl)silane and the absence of the expected tris(trimethylsilyl)silane can be reasonably explained by the following reactions:



The reaction of tris(trimethylsilyl)silyllithium and tris(trimethylsilyl)silane, affording a *ca.* 90% yield of tetrakis(trimethylsilyl)silane[10] supports this mechanism, and, therefore, a yield of greater than 50% of 9-fluorenecarboxylic acid suggests that fluorene is also metalated by other lithium species.

The relative reactivity of I

Comparative metalation reactions[11] and kinetic studies[12] have recently been used to estimate the relative reactivity of Group IVB lithium compounds. Although treatment of tris(trimethylsilyl)silyllithium (I) with fluorene presumably involves cleavage of the silicon–silicon bonds together with metalation by other lithium species, it was of interest to compare the relative reactivity of a THF solution of this compound with that of other silyllithiums. The results are summarized in Table 1.

TABLE 1

METALATIONS OF FLUORENE[11]

All compounds were allowed to metalate fluorene under identical conditions of time, temperature and concentration of reagents, followed by carbonation to produce 9-fluorenecarboxylic acid.

R_3SiLi	Yield of 9-fluorenecarboxylic acid (%)		
	Run 1	Run 2	Average
Ph_3SiLi	44.5	37.7	41.1
$Ph_3SiSiPh_2Li$[a]	44.6	39.8	42.2
$[(CH_3)_3Si]_3SiLi$[b]	51.0	44.4	47.7
$[H(CH_3)_2Si]_3SiLi$[c]	54.0	52.4	53.2
$Ph(CH_3)_2SiLi$	61.6	54.7	58.1
Ph_2CH_3SiLi	65.2	57.4	61.3

[a] A third run with this reagent gave a yield of 20.3%. [b] See Experimental. [c] Ref. 13.

From the data given in Table 1, it appears that the reactivity of pentaphenyldisilanyllithium is about equal to that of triphenylsilyllithium. However, the reaction of this compound, a polysilane, and fluorene is presumably similar to that of I, involving silicon–silicon bond cleavage and metalation by other lithium species. The reaction of tris(dimethylsilyl)silyllithium and fluorene is probably even more complicated because of the reactive Si–H bonds[14].

TABLE 2

THE RATE OF DECOMPOSITION OF I IN THF

Determination No.	Time (h)	Molarity (mole/liter)	$k_1 \times 10^{-3}$ (h^{-1})
1	0	0.198	
2	23	0.200	[a]
3	71	0.196	0.41
4	99	0.189	1.3
5	124	0.183	1.3
6	148	0.177	1.3
7	171	0.172	1.3
8	242	0.162	0.82
9	650	0.100	1.2
10	1202	0.020	0.33

[a] No rate constant was calculated because the concentration apparently increased.

A kinetic investigation of the rate of reaction of compound I with THF at room temperature was also undertaken by periodically titrating an aliquot of the silyllithium solution using the procedure of double titration[15]. The results are tabulated in Table 2 (see *Experimental*) and the first-order rate constant is given in Table 3.

A plot of time against the logarithm of molarity (Fig. 1) reveals that the de-

TABLE 3

FIRST ORDER RATE CONSTANTS FOR THE REACTION OF SOME SILYLLITHIUM COMPOUNDS WITH THF[12]

The first-order rate constants were determined using the initial linear portions of the curves (plot of the logarithm of molarity against time).

Reagent	$k \times 10^{-3}$ (h^{-1})
$[H(CH_3)_2Si]_3SiLi$[a]	0
Ph_3SiLi	0.84
$[(CH_3)_3Si]_3SiLi$[b]	1.3
$Ph(CH_3)_2SiLi$	1.4
$Ph_2(CH_3)SiLi$	2.1

[a] No change was observed after 400 h[13]. [b] See Experimental.

composition of I follows pseudo first-order kinetics up to *ca.* 900 hours at which time the rate increases considerably. The deviation, observed with all of the compounds listed in Table 3, has been attributed to a possible catalytic effect of one of the reaction products[12].

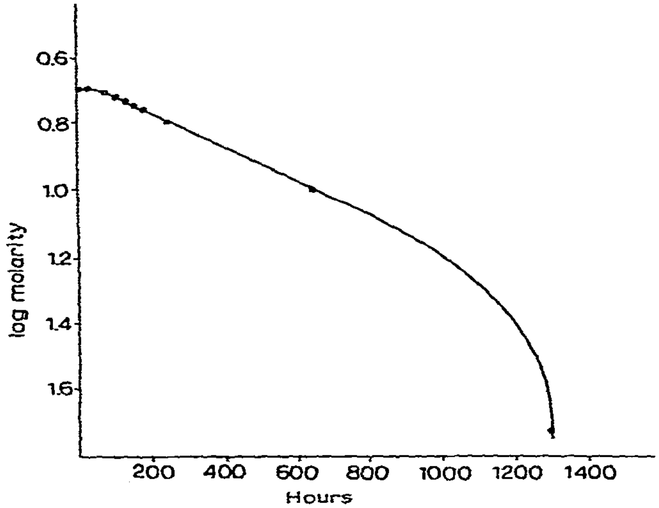
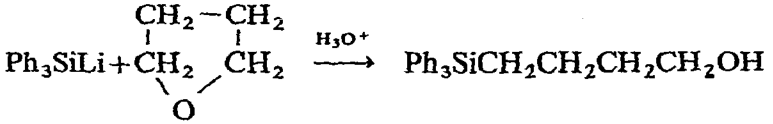


Fig. 1. Log molarity *vs.* time for tris(trimethylsilyl)silyllithium (I).

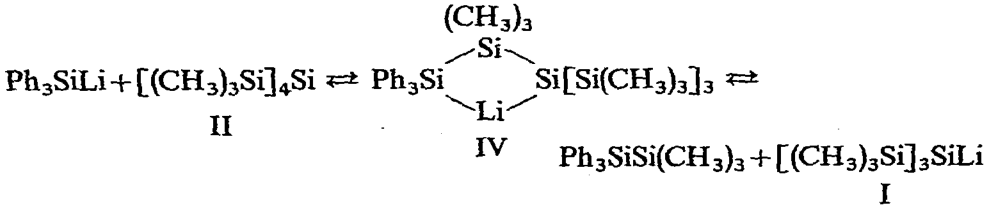
In a similar manner as its reaction with fluorene, the treatment of I with THF probably involves, in addition to ring opening, cleavage of the silicon–silicon bonds to give other lithium species. For instance, the reaction of I and THF afforded compound II and a liquid mixture of two compounds (determined by VPC). The IR spectrum of this mixture showed a strong absorption at 5.75 μ (probably C=O), and medium absorptions at 9.45 μ and 9.7 μ (Si–O): there were no peaks indicative of C–OH. Moreover, it is not known whether all of the other compounds listed in Table 3 undergo reaction by the same mechanism or afford the same types of products as the reaction of triphenylsilyllithium and THF[16]:



Results obtained by the metalation and kinetic studies indicate the following order of decreasing reactivity*: $Ph_2(CH_3)SiLi \gg Ph(CH_3)_2SiLi > [H(CH_3)_2Si]_3SiLi > [(CH_3)_3Si]_3SiLi > Ph_3SiLi \approx Ph_3SiSiPh_2Li$. The greater reactivity observed for diphenylmethylsilyllithium as opposed to dimethylphenylsilyllithium is surprising since the reverse order would be expected on the basis of the electronic effect of the substituents. A sequence based on cleavage reactions of the silicon–silicon bond is in agreement with theoretical expectations (ref. 18; see also ref. 19):

$$Ph(CH_3)_2SiLi > Ph_2CH_3SiLi > Ph_3SiLi$$

Since different disilanes were involved, the reactivity of the silicon–silicon bond was assumed to be constant with varying substituents. On the basis of this assumption, a similar investigation was undertaken to determine the relative reactivity of triphenylsilyllithium and I. To achieve this objective, the reaction below seemed suitable for the following reasons: (1) the reactants and products are very soluble and stable in THF; (2) secondary cleavage reactions to give other silyllithium compounds, for example, trimethylsilyllithium and bis(trimethylsilyl)silyldilithium, are quite unlikely because of their high reactivity; (3) the forward and reverse reactions presumably proceed through the same intermediate, IV**, and therefore, steric factors involved in these reactions are about the same.



When compound II was treated with triphenylsilyllithium, a 70% yield of 1,1,1-trimethyl-2,2,2-triphenyldisilane was isolated. The reaction was followed by VPC of a hydrolyzed aliquot of the reaction mixture and there appeared to be no change in the relative ratios of tris(trimethylsilyl)silane (III) and tetrakis(trimethylsilyl)silane (II) after *ca.* 36 hours. The reverse reaction, between compound I and 1,1,1-trimethyl-2,2,2-triphenyldisilane, afforded a 75% recovery of the disilane. It appears that no appreciable equilibria exist and that triphenylsilyllithium is more reactive than compound I.

DISCUSSION

Although the results obtained by these methods are not definitive, they seem to imply, however, that the reactivity of compound I is comparable to or even less

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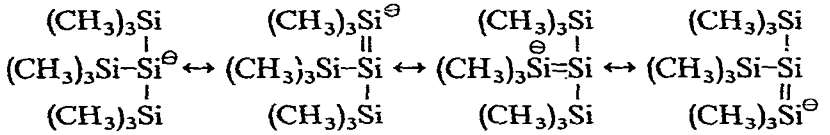
* The same order of reactivity was observed in chloride displacement reactions from n-butyl chloride[17].

** Similar pentacovalent intermediates have been proposed[20] for the coupling reactions of an RLi and 1-NpPhMeSiX (where X is a poor leaving group, H or F).

than that of triphenylsilyllithium. Secondary cleavage reactions of the silicon–silicon bond and subsequent reaction by presumably more reactive, less branched species were evident in reactions involving THF and fluorene. Due to their presence, the reactivity of I is undoubtedly somewhat less than the experimental data suggest. In the treatment of triphenylsilyllithium with II, which indicated a lower order of reactivity for I, the reactivity of the silicon–silicon bonds of the polysilane compounds, II and 1,1,1-trimethyl-2,2,2-triphenyldisilane, were assumed to be about equal.

π-Bond in I

The stability of triphenyl- and other phenylated silyllithium compounds has been attributed to delocalization of the negative charge over the aromatic ring(s) whereas trialkylsilyllithiums have at most only a transitory existence[5,6]. A reason for the enhanced stability of I becomes apparent if one compares its structure with that of the reactive trimethylsilyllithium compound. On the basis of inductive effects alone, one would expect trimethylsilyllithium to be less reactive than I since a trimethylsilyl group is a better electron donor than a methyl group[1]. However, a unique type of conjugation is possible for compound I, but not trimethylsilyllithium, involving delocalization of the negative charge over the vacant d orbitals on the adjacent silicon atoms (d_π–p_π bonding):

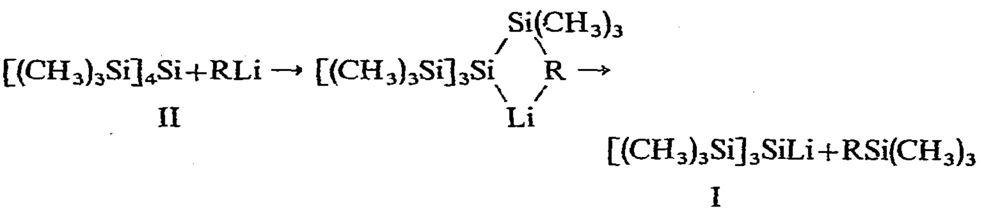


$$(CH_3)_3Si{-}\overset{(CH_3)_3Si}{\underset{(CH_3)_3Si}{Si^{\ominus}}} \leftrightarrow (CH_3)_3Si{-}\overset{(CH_3)_3Si^{\ominus}\,\|}{\underset{(CH_3)_3Si}{Si}} \leftrightarrow (CH_3)_3\overset{\ominus}{Si}{=}\overset{(CH_3)_3Si}{\underset{(CH_3)_3Si}{Si}} \leftrightarrow (CH_3)_3Si{-}\overset{(CH_3)_3Si}{\underset{\|\,(CH_3)_3Si^{\ominus}}{Si}}$$

This conjugative ($-T$) effect requires the multiple bonding of the vacant $3d$ orbitals of the peripheral silicon atoms (the electron acceptors) with the $3p$ orbital of the lithium-bearing silicon atom (the electron donor). As a consequence, it is not surprising that compound I cannot be prepared by the reaction of II and lithium metal which would require the formation of the very reactive trimethylsilyllithium[5,6]:

$$II + Li \not\rightarrow I + (CH_3)_3SiLi$$

The formation of I, on the other hand, by the reactions of II and RLi ($R = CH_3$[4], Ph[4], and Ph_3Si) compounds, probably involves nucleophilic attack by the R group on a peripheral silicon atom, followed by the elimination of the tris(trimethylsilyl)silyl group via a pentacovalent intermediate, giving stable products:



$$\underset{II}{[(CH_3)_3Si]_4Si} + RLi \rightarrow [(CH_3)_3Si]_3Si\overset{Si(CH_3)_3}{\underset{Li}{\;\;R}} \rightarrow \underset{I}{[(CH_3)_3Si]_3SiLi} + RSi(CH_3)_3$$

The stability of a series of silyllithium compounds, based on their ease of formation by the reaction of the respective polysilane with methyllithium, suggests the following order of decreasing reactivity:

$$(CH_3)_3SiSi(CH_3)_2Li^{10} > [(CH_3)_3Si]_2SiCH_3Li^{4} > [(CH_3)_3Si]_3SiLi$$

The parallelism between the number of trimethylsilyl groups bonded to the silicon atom and the ease of formation of the silanion is further evidence for dative (d_π–p_π) bonding.

Spectral properties of I

The ultraviolet and NMR spectra of I are in agreement with the proposed dative (d_π–p_π) bonding.

The ultraviolet spectrum (THF) consists of bands at λ_{max} 295 mμ ($\varepsilon \sim 22{,}000$), 370 m$\mu$ ($\varepsilon \sim 10{,}000$) and a shoulder at 236 mμ ($\varepsilon \sim 6{,}000$) whereas its derivatives, compounds II and III, showed no absorption (cyclohexane) above 210 mμ[21]. Undoubtedly, this marked bathochromic shift implies considerable resonance stabilization of the excited state[22]. Thus, it is suspected that similar resonance also exists, but to a lesser extent, in the ground state[22]. The tailing of the 370 mμ band into the visible is probably responsible for the greenish-yellow color rather than the presence of any impurity. The ^{1}H NMR spectrum of I (THF), consisting of a singlet at τ 9.93 ppm, represents a 0.2 ppm upfield chemical shift with respect to the methyl protons of tris(trimethylsilyl)silane (τ 9.73 ppm). In view of the ultraviolet spectral data, the small diamagnetic shielding of the silicon-methyl protons of I seems to be associated with this type of conjugation (d_π–p_π bonding).

The ultraviolet and NMR spectra of triphenylsilyllithium which showed similar bathochromic and diamagnetic shifts have been explained in terms of dative (p_π–p_π) bonding involving delocalization of the negative charge over the phenyl rings[23].

EXPERIMENTAL

Tetrakis(trimethylsilyl)silane (II) was prepared by the published procedure[8,9]. Fluorene was purchased from Eastman Organic Chemicals. Activated alumina (chromatographic grade, 80–200 mesh) was obtained from Matheson, Coleman and Bell. Lithium in the form of wire from Lithium Corporation of America, contained *ca.* 0.1% of sodium. The tetrahydrofuran (THF) was purified by reflux over sodium wire, distillation into lithium aluminum hydride, and distillation from the hydride immediately before use. The pipettes and flasks were baked in an oven at 140° and flushed with a stream of nitrogen until cool. All melting and boiling points are uncorrected.

The infrared spectra were determined using a Perkin–Elmer Model 21 spectrophotometer. The ^{1}H NMR spectrum was measured with a Varian HR-60 spectrometer operating at 60 MHz and the ultraviolet spectrum was determined with a Beckman DK 2A spectrophotometer. Vapor phase chromatography (VPC) was carried out with a F and M Model 500 gas chromatograph using a 18 in. $\times \frac{1}{4}$ in. column packed with silicone gum rubber SE 30 on Chromosorb W (1 : 20).

Compound II was routinely identified by VPC and IR, because of the difficulties of obtaining reproducible melting points on an analytical sample[9].

General procedure for the preparation of tris(trimethylsilyl)silyllithium (I)

Methyllithium[24] was freshly prepared in ether (~70%) and the solution was decanted from the excess lithium under nitrogen into an addition funnel. Double titration using allyl bromide[15] gave the concentration of alkyllithium solution and the relative amount of alkoxide base. Only solutions in which the amount of alkoxide base was relatively low (*ca.* 2 equivs. or less per 15 equivs. of total base) were considered satisfactory for synthetic purposes.

Compound I was prepared by stirring a THF/ether (4/1) solution of tetrakis(trimethylsilyl)silane (II) and a 10% molar excess of methyllithium at room temperature until VPC of a hydrolyzed aliquot indicated an area ratio of tris(trimethylsilyl)silane (III)*/II of at least 100/1. In general, this condition was satisfied within 24 h; if not, a 10% molar excess of methyllithium was added and the reaction mixture was continuously stirred at room temperature. The pale greenish-yellow solution was transferred to an addition funnel under nitrogen subsequent to the removal of ether by distillation. The concentration was determined by a double titration technique using allyl bromide[15].

Reaction of I and fluorene

To 13.5 g (0.08 mole) of fluorene in 50 ml of THF was added at one time 525 ml of 0.154 *M* solution of compound I (0.08 mole). The reaction mixture immediately turned orange and was stirred overnight at room temperature. Color Test I[25] was positive** and the reaction mixture was carbonated by pouring onto a Dry Ice/ether slurry. After allowing the mixture to warm to 0°, dilute hydrochloric acid was added. The organic layer was separated and the aqueous layer extracted several times with ether. The combined ethereal layers were extracted with 400 ml of 5% sodium hydroxide in several portions. The basic extract was boiled to remove traces of THF, then acidified with 10% hydrochloric acid. Filtration afforded a solid product which was recrystallized from glacial acetic acid to give 12.3 g of crude 9-fluorenecarboxylic acid, m.p. 223–226°. A second recrystallization from the same solvent gave 11.9 g (70%) of pure acid, m.p. 228–230° (mixed m.p.). In addition, about 2 g of an insoluble solid was obtained.

The organic layer was dried over sodium sulfate prior to the removal of solvents under reduced pressure. The residual oil was chromatographed on a column of alumina. Elution with petroleum ether (b.p. 60–70°) afforded 10.9 g (81.5%) of II (identified by VPC and IR), subsequent to crystallization from acetone.

A repeat of this reaction gave an 83% yield of the acid, m.p. 228–230° (mixed m.p.).

General procedure for comparative metalation reactions of I

To 8.3 g (0.05 mole) of fluorene in 380 ml of THF, cooled to 0° with an ice/salt bath, was added at one time 140 ml of a 0.352 *M* solution of compound I (0.05 mole). The solution was stirred for 1.5 h with the temperature maintained between 0° and 5°, prior to carbonation by addition to a Dry Ice/ether slurry. After allowing the mixture to warm to 0°, dilute hydrochloric acid was added. The organic layer was separated and the aqueous layer extracted several times with ether. The combined ethereal

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* The amount of I was determined as III, the hydrolysis product.

** Unlike other silyllithium compounds, compound I gives a negative Color Test I using a few drops of a 0.2% solution of iodine in glacial acetic acid as the oxidizing agent. However, a positive test is given by this compound when a 20–30% solution of iodine in glacial acetic is used[4].

layers were extracted with 400 ml of 5% sodium hydroxide in several portions. The basic extract was boiled to remove traces of THF, and acidified with 10% hydrochloric acid. Filtration afforded a solid product which after two recrystallizations from glacial acetic acid gave 5.2 g (51%) of 9-fluorenecarboxylic acid, m.p. 228–230° (mixed m.p.).

Another experiment was carried out employing 150 ml of a 0.28 *M* solution of compound I (0.042 mole) and 6.92 g (0.042 mole) of fluorene. After three recrystallizations from glacial acetic acid, 3.9 g (44.4%) of 9-fluorenecarboxylic acid, m.p. 229–231° (mixed m.p.) was obtained.

Reaction of I and THF

A solution of compound I (0.047 mole) in 275 ml of THF was heated at the reflux temperature for 4 days. After this time, the reaction mixture was hydrolyzed by addition to a mixture of crushed ice acidified with 1 *N* hydrochloric acid. The organic layer was separated and dried over sodium sulfate. Subsequent to the removal of solvents under reduced pressure, the residual oil was chromatographed on a column of alumina. Elution with petroleum ether (b.p. 60–70°) gave a small amount of a solid, identified by VPC as compound II.

Further elution with ethyl acetate followed by distillation of the combined fractions afforded a liquid, b.p. 175–180°/13 mm. VPC indicated the presence of two compounds in approximately equal amounts. An IR spectrum of the liquid mixture showed the following absorptions in μ*: 3.4 (m), 3.45 (m), 5.75 (s), 6.95 (w), 7.2 (w), 7.32 (w), 8.05 (s), 9.45 (m), 9.70 (m), 12.0 (s), and 13.4 (w).

The rate of decomposition of I in THF

The rate of decomposition of I in THF was determined at room temperature by periodically withdrawing a 5 ml aliquot of the solution and determining the concentration by double titration using allyl bromide[15]. The change in molarity as a function of time and the first-order rate constant for each consecutive determination are given in Table 2.

The decomposition of I in THF was found to follow pseudo first-order kinetics from 0.196 to 0.100 (see fig. 1). The low value, 0.82×10^{-3} h^{-1}, for determination no. 8 is probably due to experimental error. The average rate constant was calculated to be 1.3×10^{-3} h^{-1} (using *k* values for determinations 4, 5, 6, 7 and 9).

The ultraviolet spectral determination of I

Compound I was prepared in the usual manner by the reaction of II and methyllithium. Subsequent to a complete reaction, ether was removed by distillation and the silyllithium solution was transferred under nitrogen to an addition funnel. VPC of a hydrolyzed aliquot indicated an area ratio of III/II of *ca.* 150/1. A few milliters of the silyllithium solution was diluted to the desired concentration with THF in a nitrogen-filled dry box. The quartz ultraviolet cell was filled with the silyllithium solution and sealed with paraffin wax. The spectrum of this solution showed bands at λ_{max} 370 mμ ($\varepsilon \sim 10{,}000$), 295 m$\mu$ ($\varepsilon \sim 22{,}000$) and a shoulder at 236 mμ ($\varepsilon \sim 6{,}000$).

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* Letters indicate the relative intensities of absorption bands: s = strong, m = medium, w = weak.

The NMR spectral determination of I

Compound I was prepared in the usual manner. The silyllithium solution was concentrated by distillation to *ca.* 2 *M* (determined by double titration using allyl bromide)[15]. This solution was transferred under nitrogen to an NMR capillary tube and sealed. The NMR spectrum of the THF solution of I, using cyclohexane as the internal standard, contained a singlet at τ 9.93 ppm. Except for the expected multiplets due to THF*, there were no other absorptions present.

Reaction of triphenylsilyllithium and II

Triphenylsilyllithium was prepared in THF by the cleavage reaction of lithium and hexaphenyldisilane[27].

To 10 g (0.03 mole) of compound II in 150 ml of THF was added triphenylsilyllithium (0.03 mole) and the reaction mixture was stirred for 18 h at room temperature. After this time VPC of a hydrolyzed aliquot of the purple-colored solution indicated an area ratio for III/II of 9/1. There appeared to be no change in this ratio after stirring for an additional 20 h. The reaction mixture was hydrolyzed by addition to a mixture of ice and 1 *N* hydrochloric acid. Subsequent to the separation and drying of the organic layer over sodium sulfate, the solvents were removed under reduced pressure to give an oil. From this oil, there crystallized 8 g of impure 1,1,1-trimethyl-2,2,2-triphenyldisilane. Purification by crystallization from 95% ethanol gave 6.5 g (70%)** of the pure compound, m.p. 107–109° (mixed m.p.).

Distillation of the residue afforded 3.1 g (45%)** of pure III, b.p. 90–95°/10 mm, n_D^{20} 1.4901 (lit.[4] b.p. 80–83°/8 mm, n_D^{20} 1.4891), and 2.7 g of a liquid residue. VPC of this liquid showed only the presence of compounds III and II (area ratio of 7 : 10). There was no evidence for triphenylsilane, triphenylsilanol or hexaphenyldisiloxane.

Another experiment was carried out, using a procedure identical to that above, but the reaction mixture was stirred overnight. From the reaction mixture there was obtained 51% of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 107–109° (mixed m.p.), and 52% of III, b.p. 94–96°/10 mm, n_D^{20} 1.4891. Some unreacted compound II was detected by VPC.

Reaction of I and 1,1,1-*trimethyl*-2,2,2-*triphenyldisilane*

Compound I (0.016 mole) and 5.56 g (0.016 mole) of 1,1,1-trimethyl-2,2,2-triphenyldisilane dissolved in 125 ml of THF were stirred overnight at room temperature. After this time, the reaction mixture was hydrolyzed by addition to a mixture of ice and 1 *N* hydrochloric acid. The organic layer was separated and dried over sodium sulfate prior to the removal of solvents under reduced pressure. The residual oil was distilled to give 3 g (73%) of III, b.p. 99–103°/17 mm, n_D^{20} 1.4889.

The residual solid was chromatographed on a column of alumina. Elution with petroleum ether (b.p. 60–70°) gave 4 g (75%) of unreacted 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 107–109° (mixed m.p.), and 1 g (19%) of II (identified by its IR spectrum and VPC). There was no evidence for triphenylsilane, triphenylsilanol nor hexaphenyldisiloxane.

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* The spectrum was compared with that of a sample of pure THF[26].

** The yield is based on the amount of unrecovered II, assuming the following reaction:

$$Ph_3SiLi + II \xrightarrow{H_3O^+} III + Ph_3SiSi(CH_3)_3$$

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