# Photolysis of Polymeric Organosilicon Systems. 4. Photochemical Behavior of Poly[*p*-(disilanylene)phenylene]

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Poly[*p*-(1,2-diethyldimethyldisilanylene)phenylene] (1) and poly[*p*-(1,2-dimethyldiphenyldisilanylene)phenylene] (2) were synthesized by the condensation reaction of 1,4-bis(chloroethylmethylsilyl)benzene and 1,4-bis(chloromethylphenylsilyl)benzene with sodium metal in toluene. The photochemical behavior of 1 and 2 has been examined in solutions and in solid films. Irradiation of 1 and 2 with a low-pressure mercury lamp in solutions resulted in homolytic scission of silicon–silicon bonds, followed by the formation of silicon–carbon unsaturated compounds and hydrosilanes. The former compounds could be trapped by methanol. Irradiation of thin solid films of 1 in air led to the formation of photoproducts containing Si–OH and Si–O–Si groups and a trace of an Si–H group, while 2 afforded the products which involve the Si–H group, in addition to the Si–OH and Si–O–Si groups. A mechanism of the photodegradation of 1 and 2 is proposed.

## Introduction

It is well-known that $\pi$-electron system-substituted disilanyl groups act as chromophore. In fact, aryl-, alkenyl-, and alkynyl-substituted organodisilanes are photoactive under ultraviolet irradiation, and their photochemical behavior has been extensively studied.[1] However, little interest has been shown in the photochemistry of polymers bearing $\pi$-electron system-substituted disilanyl units.[2,3]

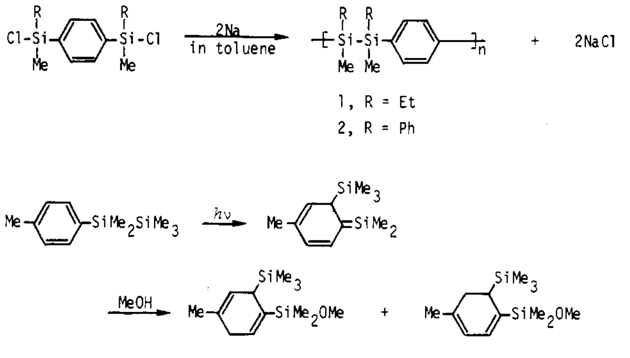
Recently, we have found that UV irradiation of polysiloxanes containing phenyl(trimethylsilyl)siloxy units in the polymer backbone leads to homolytic scission of silicon–silicon bonds and results in the formation of cross-linked solid substances.[4] As a part of an investigation concerning the photochemistry of polymeric organosilicon compounds involving $\pi$-electron system-substituted disilanyl units, we have synthesized *p*-(disilanylene)phenylene polymers and examined their photochemical behavior in solutions and in solid films.[5]

## Results and Discussion

**Synthesis of Poly[*p*-(1,2-diethyldimethyldisilanylene)phenylene] (1) and Poly[*p*-(1,2-dimethyldiphenyldisilanylene)phenylene] (2).** First, we attempted to prepare poly[*p*-(tetramethyldisilanylene)phenylene] by the condensation of 1,4-bis(chlorodimethylsilyl)benzene with sodium metal in toluene. However, the polymers thus obtained were mainly insoluble and intractable white solid materials. This may be ascribed to the high crystallinity of the polymers. In order to reduce the crystallinity, we used 1,4-bis(chloroethylmethylsilyl)benzene and 1,4-bis(chloromethylphenylsilyl)benzene as the starting monomers. These compounds could readily be prepared by a two-step synthesis from *p*-phenylene(dimagnesium bromide) and the corresponding diethoxysilane derivatives.

The reaction of these monomers with sodium dispersion, prepared in toluene, at 70–90 °C under a nitrogen atmosphere afforded poly[*p*-(1,2-diethyldimethyldisilanylene)phenylene] (1) and poly[*p*-(1,2-dimethyldiphenyldisilanylene)phenylene] (2), respectively, in good yields (Scheme I).

Scheme I



Both polymers 1 and 2 are soluble in common organic solvents, melt without decomposition, and can be drawn into the fibers. Molecular weights of polymers 1 and 2 determined by gel permeation chromatography with tetrahydrofuran as the eluant, after purification by reprecipitation from benzene–ethanol and benzene–isopropyl alcohol, showed a broad monomodal molecular weight distribution. Polymers with molecular weights of 23 000–34 000 are always obtained, if fine sodium particles are used and the reactions are carried out at 70–90 °C. The condensation in refluxing toluene does not produce polymers with higher molecular weight.

The $^1$H NMR chemical shifts of polymers 1 and 2 are only slightly dependent of the molecular weight. Thus,

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† On leave from Chenguang Research Institute of Chemical Industry, The People's Republic of China.

(1) (a) Ishikawa, M. *Pure Appl. Chem.* **1978**, *50*, 11. (b) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

(2) Ishikawa, M.; Imamura, N.; Miyoshi, N.; Kumada, M. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 657.

(3) Aryl-substituted polysilane high polymers, see, for examples; (a) Trujirro, R. E. *J. Organomet. Chem.* **1980**, *198*, C27. (b) West, R.; David, L. D.; Djurovich, P. I.; Stearly, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352. (c) Trefonas, P.; Djurovich, P. I.; Zhang, X.-H.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 819, 823. (d) Zhang, X.-H.; West, R. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 159, 225. (e) Zhang, X.-H.; West, R. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 479.

(4) Nate, K.; Ishikawa, M.; Imamura, N.; Murakami, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1552.

(5) Ishikawa, M.; Ni, H.; Matsusaki, K.; Nate, K.; Inoue, T.; Yokono, H. *J. Polym. Sci. Polym. Lett. Ed.* **1984**, *22*, 669.

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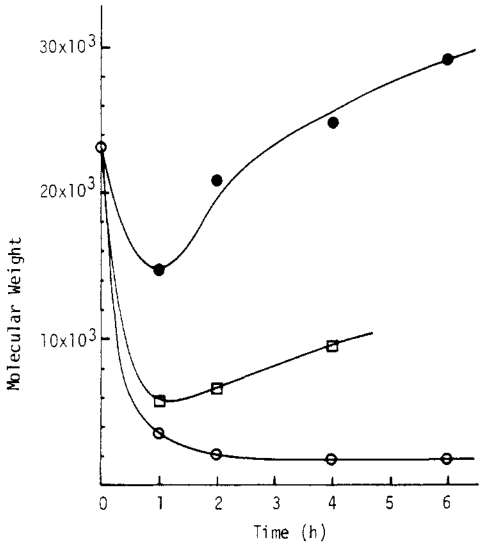


**Figure 1.** Plot of molecular weights of products vs. irradiation time for the photolysis of **1**: (●) irradiation in benzene; (□) irradiation in toluene; (○) irradiation in the presence of methanol in benzene.

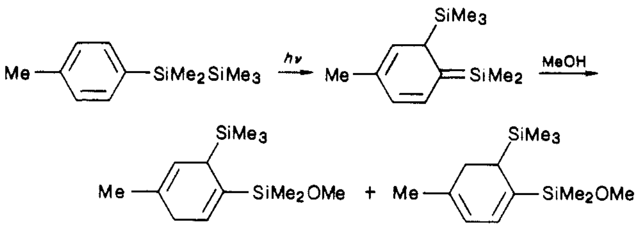
the $^1H$ NMR spectrum of polymer **1** whose molecular weight is determined to be 34 000 shows three sharp signals at δ 0.34, 0.94, and 7.28, due to MeSi, EtSi, and phenyl ring protons, while polymer **1** with a molecular weight of 23 000 reveals these resonances at δ 0.32, 0.93, and 7.25, respectively. Similarly, polymer **2** with molecular weight of 27 500 exhibits sharp resonances at δ 0.62, 7.28, and 7.35, attributed to MeSi and phenyl ring protons. For polymer **2** with lower molecular weight ($\bar{M}_w$ 18 000), these resonances appear at δ 0.60, 7.16, and 7.23.

Polymers **1** ($\bar{M}_w$ 34 000) and **2** ($\bar{M}_w$ 27 500) show characteristic strong UV absorption bands at 262 and 254 nm, respectively, significantly red-shifted relative to phenylpentamethyldisilane which exhibits an absorption band at 231 nm (ε 10 900).[6-8] Polymers **1** ($\bar{M}_w$ 23 000) and **2** ($\bar{M}_w$ 18 000) with lower molecular weights also show these bands at the same positions. No significant shifts were observed in both cases. Extinction coefficient (ε) per disilanylenephenylene unit is calculated to be 16 000 for polymer **1** and 19 000 for polymer **2**.

**Photolysis of Polymers 1 and 2 in Solution.** When a benzene solution of polymer **1** was photolyzed upon irradiation with a 6-W low-pressure mercury lamp for 2 h, soluble photodegradation products were produced. In order to learn the influence of irradiation time on the molecular weight of photodegradation products, we photolyzed benzene solutions containing **1** with a molecular weight of 23 000 for a definite time under the same conditions, and the molecular weights of the resulting photoproducts were determined by GPC. As can be seen in Figure 1, the molecular weight of the photoproducts decreased in the early stages of the photochemical reaction, passed through a minimum value of 14 500 after 1 h, and then increased gradually with increasing reaction time (29 000 after 6 h and 37 000 after 12 h[9]), indicating that some cross-linking reactions occurred during the photolysis. $^1H$ NMR spectra of the resulting photoproducts show very broad resonances for MeSi, EtSi, and phenyl ring protons. In addition, a multiplet resonance with low intensity due to an Si–H proton is observed at δ 4.2 in all the photoproducts. UV spectra of the products show disappearance of the original strong band at 262 nm, and IR spectra reveal a band with medium intensity at 2120 $cm^{-1}$ attributed to the stretching frequencies of an Si–H.

We next carried out the photolysis of **1** in the presence of an 8-fold excess of methanol in benzene. In contrast to the photolyses in the absence of methanol, the molecular weight of the photoproducts decreased continuously with increasing reaction time and finally reached a constant value ($\bar{M}_w$ 1800) after 4-h irradiation. The $^1H$ NMR spectrum of the photoproducts shows signals at δ 3.4 and 4.2, due to $CH_3$–O and Si–H protons, in addition to the broad signals corresponding to MeSi, EtSi, and phenyl ring protons. The resonances of low intensity at δ 2.2 and 6.2 assigned tentatively as cyclohexadienyl ring protons are also observed. The intensity of these proton signals reached a maximum value after 2-h irradiation. The cyclohexadienyl ring protons, however, completely disappeared after 4-h irradiation, while the resonances due to the $CH_3$–O and Si–H protons remained unchanged. Presumably, aromatization of the cyclohexadienyl ring occurred.

Assuming that our assignment for the cyclohexadienyl ring protons is correct, the result indicates that rearranged silicon–carbon unsaturated compounds are formed in the photodegradative processes. We have demonstrated that this type of silenes can be produced by the photolyses of aryldisilanes, and the resulting silenes react with alcohol to give 1,6-disilyl-substituted cyclohexadiene derivatives.[1] For example, the photolysis of *p*-tolylpentamethyldisilane in the presence of methanol gives 1-(methoxydimethylsilyl)-4-methyl-6-(trimethylsilyl)-1,3-cyclohexadiene and -1,4-cyclohexadiene as main products.[10] The $^1H$ NMR spectra of both compounds reveal signals due to the cyclohexadienyl ring protons at the same regions as above.



The photorearranged silene intermediates, however, are involved only as minor products for the present polymeric systems. In fact, the ratio of the cyclohexadienyl group to the disilanylenephenylene unit in the photoproducts, which shows a maximum value of the cyclohexadienyl ring protons, is calculated to be approximately 1:19 by $^1H$ NMR spectroscopic analysis.

When a benzene solution of **1** containing methanol-$d_1$ was photolyzed under the same conditions, the products containing both $CH_3$–O and Si–H groups were obtained. The IR spectrum of the product shows no absorption due to an Si–D stretching frequencies, indicating that no direct reaction of the photoexcited **1** with methanol is involved. The relative ratio of Si–H to $CH_3$–O to $[Me(Et)SiSiMe(Et)C_6H_4]_n$ in the photoproduct obtained from 4-h irradiation of **1** is determined to be 1:1.5–2.0:3.8 (*n*). The results clearly indicate the formation of a different type of silicon–carbon double-bonded intermediates. This type of silene may be produced from homolytic scission of silicon–silicon bonds, followed by hydrogen abstraction of

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(6) Hague, D. N.; Prince, R. H. *Chem. Ind. (Milan)* **1964**, 1492.

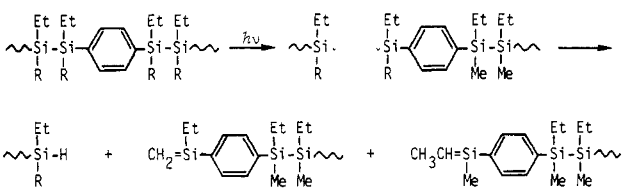
(7) Gilman, H.; Atwell, W. H.; Schwebke, G. L. *J. Organomet. Chem.* **1964**, *2*, 369.

(8) Sakurai, H.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1894.

(9) Irradiation of the polymer **1** for 6 h gave some insoluble polymers.

(10) (a) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 155. (b) Ishikawa, M.; Oda, M.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2795.

Scheme II



the resulting radical from either a methyl group or a methylene of an ethyl group on the others as shown in Scheme II. On the basis of the methoxy contents in the photoproducts, these silenes seem to be formed as main products in the polymeric systems, although this type of silene is produced only as a minor product in the photolysis of aryldisilanes.[11]

Treatment of the reaction mixture obtained from the photolysis of 1 in the presence of methanol-$d_1$ with silica gel column chromatography gave a product of molecular weight 1000. The $^1$H NMR spectrum of this product shows sharp resonances at $\delta$ 0.51–0.70 (m), 1.03–1.42 (m), 3.52, 4.73, and 7.65, attributed to MeSi, EtSi, $CH_3O$, HSi, and phenylene ring protons, respectively. In the complete decoupled $^{13}$C NMR spectrum of the product, however, a triplet due to $DCH_2Si$ could not be observed because of overlap with the resonances of other methylsilyl carbons.

The photolysis of polymer 1 in toluene under the same conditions showed a similar trend to that in benzene as shown in Figure 1. However, the molecular weights of the photoproducts were lower than those obtained from the benzene solutions. Photochemically generated radicals would undergo homolytic aromatic substitution, in competition with the formation of the silenes which leads to [2 + 2] cycloaddition or polymerization reaction. We think that the homolytic aromatic substitution on the tolyl ring would be easier than on the benzene ring. Consequently, in toluene, photodegradation products of lower molecular weights than those obtained in benzene would be produced. In fact, $^1$H NMR spectra of the photoproducts obtained from the toluene solution reveal resonances at $\delta$ 2.3 and 4.3, due to the methyl protons of a tolyl group and an Si–H proton. The ratio of the Si–H and the methyl of the tolyl group to the disilanylenephenylene unit was calculated to be approximately 1:1:11 by $^1$H NMR spectroscopic analysis.

The photolysis of polymer 2 in the absence of methanol proceeded in considerably different fashion from that of 1. Irradiation of a benzene solution of 2 resulted in a decrease of the molecular weight of the photoproducts. No increase of the molecular weight of the products with increasing reaction time was observed. Moreover, the photodegradation of 2 proceeded faster than that of 1 (Figure 2). Thus, the photolysis of a benzene solution of 2 for 1 h with a low-pressure mercury lamp led to the formation of a photoproduct of molecular weight 5900, which remained unchanged after 4-h irradiation. $^1$H NMR spectra of the products display broad signals at $\delta$ 0.6, 4.9, and 6.8–7.8, attributed to MeSi, HSi, and phenyl ring protons, respectively.

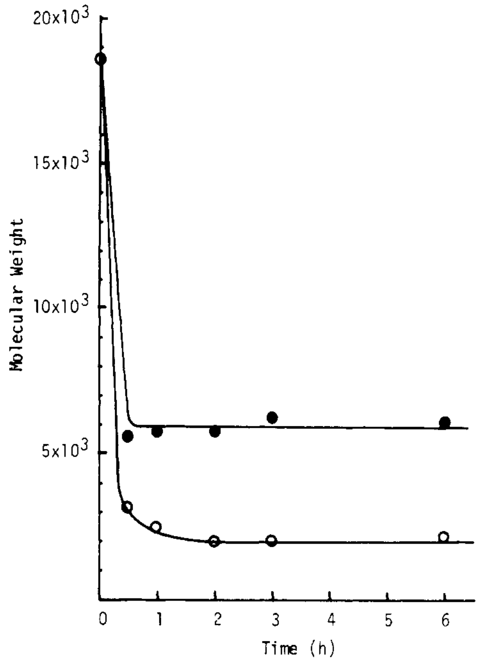
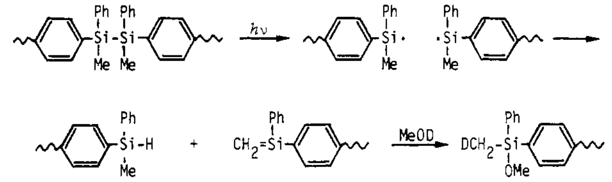


**Figure 2.** Plot of molecular weights of products vs. irradiation time for the photolysis of 2: (●) irradiation in benzene; (○) irradiation in the presence of methanol in benzene.

Scheme III



Irradiation of 2 in the presence of methanol for 1 h afforded a product of molecular weight 2000 which remained constant during further irradiation. IR and $^1$H NMR spectra show that the resulting products involve both $CH_3$–O and Si–H groups. The relative ratio of an Si–H and $CH_3$–O group to $[Ph(Me)SiSi(Me)PhC_6H_4]_n$ is calculated as being 1:1.0–1.7:2.5–3.0 ($n$).

When similar photolysis of 2 in the presence of methanol-$d_1$ was carried out, again the product whose $^1$H NMR spectrum reveals the resonance due to the Si–H proton was obtained. The relative ratio of the Si–H and $CH_3$–O protons was identical with those of the products obtained in the presence of nondeuteriated methanol. The formation of the methoxysilyl group can be understood in terms of the addition of methanol across the silicon–carbon double bonds. $^1$H NMR spectra of all photoproducts obtained from the photolyses of 2 in the presence of methanol reveal no resonances attributed to cyclohexadienyl ring protons. This indicates that photochemical degradation of polymer 2 gives no rearranged silene intermediates but produces exclusively silaethene intermediates and hydrosilanes (Scheme III). In the absence of methanol, the silenes thus formed presumably undergo cycloaddition reaction to give disilacyclobutane derivatives, or they might transform into stable compounds by other processes which are still unknown.

In order to obtain further information concerning the formation of the silenes, the products obtained from the photolysis of a benzene solution of polymer 2 in the presence of methanol-$d_1$ were treated with silica gel column chromatography. 1,4-Bis(methylphenylsilyl)benzene was isolated in 6% yield, as the first fraction eluted by a 1:1 mixture of hexane and benzene. As the second fraction,

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[11] It has been reported that the photolysis of methylpentaphenyldisilane in the presence of methanol gave a methanol adduct of $CH_2{=}SiPh_2$ in high yield;[12] however, our results obtained from the photolyses of $Ph_nMe_{6-n}Si_2$ with $n$ = 1–5 in the presence of methanol indicated that the silaethene adducts were produced only as minor products (less than 10%), but the rearranged addition products as main products.[1b,13]

[12] Boudjouk, P.; Roberts, J. R.; Gollino, C. M.; Sommer, L. H. *J. Am. Chem. Soc.* **1972**, *94*, 7926.

[13] Ishikawa, M.; Nakagawa, K.; Umetani, S.; Kumada, M., unpublished results.

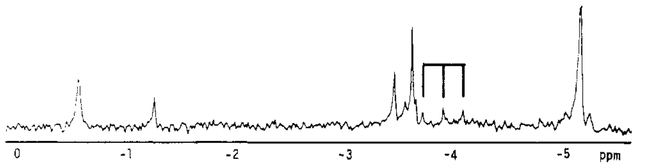

**Figure 3.** Decoupled $^{13}C$ NMR spectrum (methylsilyl region) of the photoproduct obtained from the photolysis of 2 in the presence of methanol-$d_1$ ($J_{C-D}$ = 18.3 Hz).

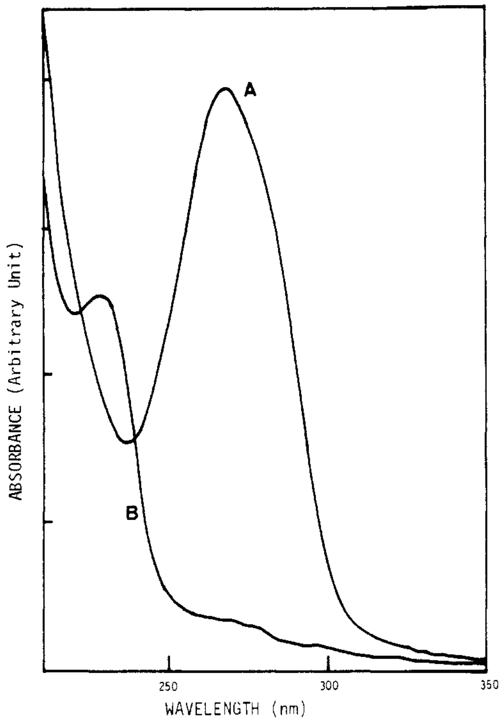

**Figure 4.** UV spectra of a thin solid film of 1: (A) before irradiation; (B) after irradition.

a product of molecular weight 1000 (by GPC) was obtained in 15% yield (wt %). The $^1H$ NMR spectrum of this fraction shows rather sharp resonances at $\delta$ 0.2–0.8, 3.50, 4.93, and 7.0–7.7 due to MeSi, $CH_3O$, SiH, and phenyl ring protons, respectively. The complete decoupled $^{13}C$ NMR spectrum of the product reveals a triplet at $\delta$ −3.89 ($J_{C-D}$ = 18.3 Hz), due to $DCH_2Si$, in addition to other MeSi carbons, indicating that methanol-$d_1$ adds across the silicon–carbon double bonds (Figure 3). The third fraction ($\bar{M}_w$ 2500), eluted by THF, was obtained in 78% yield (wt %); however, its $^1H$ NMR spectrum shows broad proton signals.

The results obtained here strongly suggest that the photodegradative processes of polymers 1 and 2 in solutions involve mainly radical scission of the silicon–silicon bonds in the polymer backbone, followed by disproportionation of the resulting radicals giving the silene intermediates and hydrosilanes.

**Photolysis of Polymers 1 and 2 in Solid Films.** The absorption spectra of polymers 1 and 2 in the solid films exhibit a broad structureless band at 262 and 254 nm, respectively. The absorption maxima of these bands are not different from those in a THF solution.

We have examined the photochemistry of the thin films of polymers 1 and 2, in order to learn whether the polymers can be used as positive deep UV resists. Thus, irradiation of thin films with a thickness of approximately 0.1 $\mu$m prepared by spin coating of a 5% toluene solution of the polymer 1 on a quartz plate in the air with a 500-W Xe–Hg lamp for 30 s gave photodegradation products, which are soluble in 2-ethoxyethanol.[14] The absorption at 262 nm observed in UV spectra of the starting films disappeared after UV irradiation, showing that the scission of the silicon–silicon bonds occured (Figure 4). IR spectra of the resulting films showed that intensity of the band at 500 $cm^{-1}$ assigned as the Si–Si stretching frequencies decreased remarkably, and strong absorption bands at 3350 ($\nu_{Si-OH}$) and 1060 $cm^{-1}$ ($\nu_{Si-O-Si}$) and a broad band at 1720 $cm^{-1}$ ($\nu_{C=O}$) appeared after UV irradiation. The fact that an only very weak absorption band at 2140 $cm^{-1}$ due to the Si–H stretching frequencies was observed (Figure 5) indicates the silyl radicals generated photochemically from the scission of the silicon–silicon bonds were scavenged by oxygen in the air. Indeed, IR spectra of the products obtained from similar photolysis under reduced pressure ($10^{-3}$ Torr) obviously show the absorption due to the Si–H stretching frequencies but the absence of $\nu_{Si-OH}$ and $\nu_{C=O}$ frequencies. The spectra, however, show the absorption due to $\nu_{Si-O-Si}$ at 1060 $cm^{-1}$. The absorption at 1060 $cm^{-1}$ may be ascribed to contamination by a trace of oxygen that could not be excluded completely during the photolysis or preparation of the solid films.

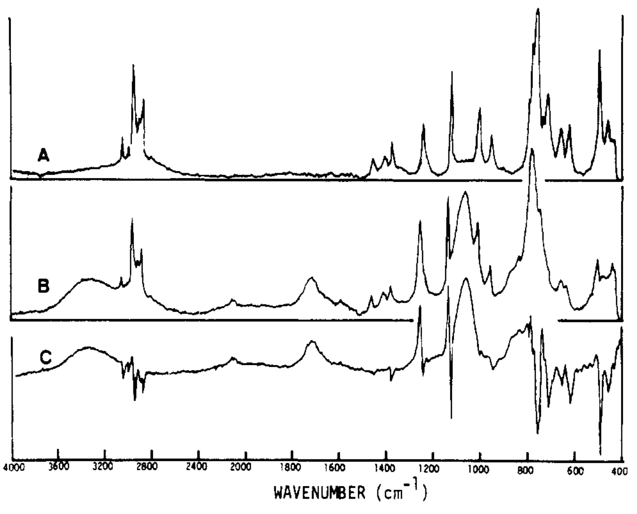

**Figure 5.** IR spectra of a thin solid film of 1: (A) before irradiation; (B) after irradiation; (C) difference spectrum between A and B.

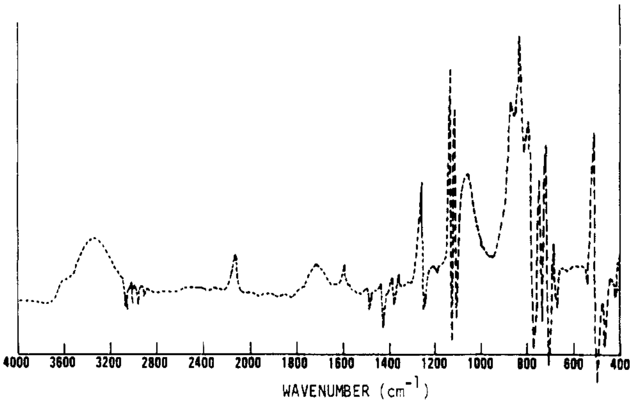

**Figure 6.** IR difference spectrum of 2 (before irradiation and after irradiation).

Irradiation of a solid film prepared from the polymer 2 in the air afforded photodegradation products that are soluble in 2-ethoxyethanol. IR spectra of the products show strong absorption bands attributed to $\nu_{Si-OH}$ and $\nu_{Si-O-Si}$. In contrast to the photoproducts from 1, these

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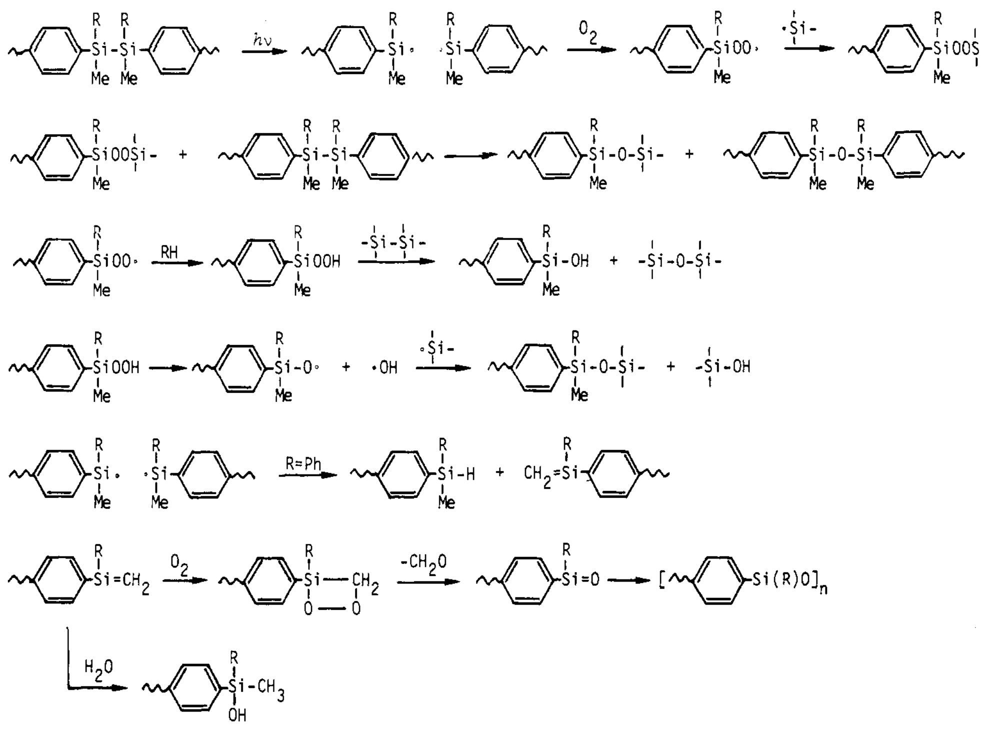
[14] A small amount of insoluble materials remained after treatment of the resulting products with 2-ethoxyethanol.

**Scheme IV**



products show the absorption due to the Si–H bond (Figure 6). This result indicates that some of the silenes would be formed in this system. The intense absorption at 254 nm in the UV spectrum again disappeared after UV irradiation, as shown in Figure 7. We suggest the photodegradation processes shown in Scheme IV for the solid films.

In conclusion, the main route for the photodegradation of polymers **1** and **2** in solid films in the air consists of radical scission of the silicon–silicon bonds, analogous to that observed in solution, but in the films, the resulting silyl radicals react with oxygen to give siloxanes and silanols as the final products. For polymer **2**, the formation of silenes that would be trapped by oxygen or moisture in the air are also involved as a minor degradative pathway. That the silene reacts with molecular oxygen to give a siloxane has been recently reported.[15]

## Experimental Section

**General Data.** $^1$H NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer in carbon tetrachloride with the use of cyclohexane as an internal standard. $^{13}$C NMR spectra were obtained on a JEOL Model JNM-GX-400 spectrometer in deuteriochloroform as a solvent. IR spectra were determined with a Nicolet FT-IR spectrometer SX-170. Mass spectra were measured on a JEOL Model JMS-D300 equipped with a JMA-2000 data processing system. Molecular weights of polymers **1** and **2** and their photoproducts were determined with a Hitachi Model 635 HPLC with a Shodex A802 and A803 column, using THF as the eluant. The data on molecular weights reported here are based on polystyrene standards.

**Solvents.** Benzene, toluene, and THF were dried over lithium aluminum hydride and distilled just before use.

**Preparation of 1,4-Bis(ethoxyethylmethylsilyl)benzene.** In a 1-L three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was placed 334 g (2.1 mol) of diethoxyethylmethylsilane and 55 g (2.3 mol) of magnesium in 200 mL of dry THF. To this was added 243 g (1.0 mol) of *p*-dibromobenzene dissolved in 300 mL of THF over a period of 4 h at room temperature. The mixture was heated to reflux for 7 h, and then ca. 300 mL of THF was distilled off. To this was added 300 mL of dry hexane, and the mixture was filtered off. The solvents were evaporated, and the residue was fractionally distilled to give 216 g (68% yield) of 1,4-bis(ethoxyethylmethylsilyl)benzene: bp 122–124 °C (1 mm); IR 1160 cm$^{-1}$; mass 310 (M$^+$); $^1$H NMR $\delta$ 0.38 (s, 6 H, MeSi), 0.80–1.30 (m, 16 H, EtSi and $CH_3CH_2O$), 3.74 (q, 4 H, $CH_2O$), 7.65 (s, 4 H, ring protons). Anal. Calcd for $C_{16}H_{30}O_2Si_2$: C, 61.87; H, 9.74. Found: C, 61.98; H, 9.81.

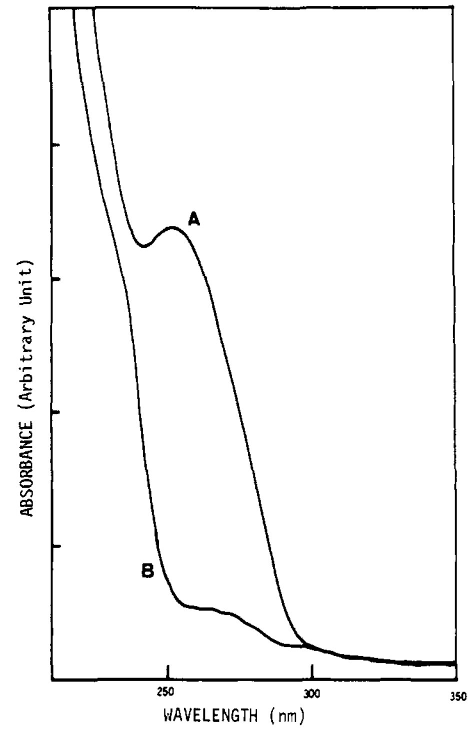


**Figure 7.** UV spectra of a thin solid film of **2**: (A) before irradiation; (B) after irradiation.

**Preparation of 1,4-Bis(chloroethylmethylsilyl)benzene.** In a 1-L flask fitted with a condenser was placed a mixture of 310 g (1 mol) of 1,4-bis(ethoxyethylmethylsilyl)benzene and 371 g (6 mol) of acetyl chloride. The mixture was heated to reflux for 6 h, and the remaining acetyl chloride and the resulting ethyl acetate were evaporated. The residue was distilled under reduced

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(15) Brook, A. G. *J. Organomet. Chem.* **1986**, *300*, 21.

pressure to give 252 g (87% yield) of 1,4-bis(chloroethylmethylsilyl)benzene: bp 126–127 °C (1 mm); mass 290 (M$^+$); $^1$H NMR $\delta$ 0.70 (s, 6 H, MeSi), 1.14 (s, 10 H, EtSi), 7.70 (s, 4 H, ring protons). Anal. Calcd for $C_{12}H_{20}Cl_2Si_2$: C, 49.46; H, 6.91. Found: C, 49.42; H, 6.85.

**Preparation of 1,4-Bis(ethoxymethylphenylsilyl)benzene.** 1,4-Bis(ethoxymethylphenylsilyl)benzene was obtained by the reaction of 246 g (1.2 mol) of diethoxymethylphenylsilane with *p*-phenylenedimagnesium bromide, prepared from 28 g (1.2 mol) of magnesium and 138 g (0.6 mol) of *p*-dibromobenzene in THF, in 78% yield: bp 211–215 °C (1 mm) (lit.[16] 187–188 °C (0.06 mm)); $^1$H NMR $\delta$ 0.76 (s, 6 H, MeSi), 1.36 (t, 6 H, $CH_3$CH$_2$O), 3.94 (q, 4 H, CH$_2$O), 7.43–7.79 (m, 14 H, phenyl ring protons and phenylene ring protons).

**Preparation of 1,4-Bis(chloromethylphenylsilyl)benzene.** A mixture of 183 g (0.45 mol) of 1,4-bis(ethoxymethylphenylsilyl)benzene and 300 g (3.8 mol) of acetyl chloride was heated to reflux for 6 h. Distillation gave 163 g (94% yield) of 1,4-bis(chloromethylphenylsilyl)benzene: bp 228–232 °C (2 mm) (lit.[17] 193–195 °C (3 mm)); $^1$H NMR $\delta$ 1.00 (s, 6 H, MeSi), 7.40–7.84 (m, 14 H, phenyl and phenylene ring protons).

**Preparation of Poly[*p*-(1,2-diethyldimethyldisilanylene)phenylene] (1).** In a 500-mL three-necked flask fitted with a stirrer, dropping funnel, and condenser was placed 5 g (0.22 mol) of sodium in 100 mL of dry toluene. The contents of the flask were heated to reflux under a nitrogen atmosphere and then stirred vigorously to prepare sodium dispersion. To this was added a solution of 15 g (0.05 mol) of 1,4-bis(chloroethylmethylsilyl)benzene dissolved in 50 mL of dry toluene over a period of 1 h at 70–90 °C. After the mixture was heated at 70–90 °C for 20 h, the remaining sodium was decomposed with a 1:1 mixture of ethanol and acetic acid. The mixture was then hydrolyzed with water. The organic layer was separated, washed with water, and filtered off. The filtrate was concentrated to give a solid polymer. The crude polymer was purified twice by reprecipitation from benzene–ethanol and then from benzene–isopropyl alcohol give a colorless white powder: mp 186–189 °C; $\bar{M}_w$ 34 000; $^1$H NMR $\delta$ 0.34 (s, 6 H, MeSi), 0.94 (s, 10 H, EtSi), 7.28 (s, 4 H, ring protons). Anal. Calcd for $C_{12}H_{20}Si_2$: C, 65.37; H, 9.14. Found: C, 65.49; H, 9.37.

**Preparation of Poly[*p*-(1,2-dimethyldiphenyldisilanylene)phenylene] (2).** In a 500-mL three-necked flask was placed sodium dispersion prepared from 15 g (0.65 mol) of sodium in 100 mL of dry toluene. To this was added 60 g (0.16 mol) of 1,4-bis(chloromethylphenylsilyl)benzene dissolved in 20 mL of dry toluene over a period of 1 h at 80–90 °C. The mixture was heated at the same temperature for 5 h and then hydrolyzed as usual. The organic layer was separated and filtered. The filtrate was concentrated, and the resulting white solid was purified twice by reprecipitation from benzene–ethanol and then from benzene–isopropyl alcohol to give 22 g (45% yield) of polymer **2**: mp 152–164 °C; $\bar{M}_w$ 27 500; $^1$H NMR $\delta$ 0.62 (s, 6 H, MeSi), 7.28 and 7.35 (m, 14 H, phenyl and phenylene ring protons). Anal. Calcd for $C_{20}H_{20}Si_2$: C, 75.89; H, 6.37. Found: C, 76.13; H, 6.56.

**Photolyses in Solutions.** The following is typical of the procedures used. After the polymer **1** ($\bar{M}_w$ 23 000) was dried in vacuo at 80 °C for 5 h, 250 mL of a benzene solution containing 1.5010 g of **1** was prepared. Then 25 mL of this solution was transferred into a reaction vessel for photolysis and irradiated with a 6-W low-pressure mercury lamp (2537 Å) at room temperature for 1 h, under a slow stream of nitrogen bubbling through the solution. The solvent benzene was evaporated, and the residue was heated at 70–80 °C in vacuo for 1 h to give 0.1489 g of the photoproducts: $\bar{M}_w$ 14 500; IR 2120 cm$^{-1}$; $^1$H NMR $\delta$ 0.30 (br s, MeSi), 0.88 (very br s, EtSi), 6.9–7.6 (m, phenylene ring protons). The same solutions were photolyzed for a definite time under the same conditions to obtain the relationship between molecular weight and irradiation time (see Figure 1). In trapping experiments, for example, a mixture of 25 mL of the above benzene solution and 0.2 mL of dry methanol was photolyzed for 2 h under the same conditions. The solvent benzene and the remaining methanol were evaporated, and the residue was heated at 70–80 °C in vacuo for 1 h to give 0.1521 g of the photoproducts: $\bar{M}_w$ 2100; IR 2120, 1090 cm$^{-1}$; $^1$H NMR $\delta$ 0.30 (br s, MeSi), 0.89 (very br s, EtSi), 2.2 (m, CH$_2$ of cyclohexadienyl ring), 3.38 (br s, MeO), 4.3 (m, HSi), 6.2 (m, olefinic protons of cyclohexadienyl ring), 7.1–7.6 (m, phenyl ring protons). The relationship between molecular weights and irradiation time is shown in Figure 1. The photolyses in toluene were carried out by using 25 mL of toluene solutions containing 0.1498 g of the polymer **1** ($\bar{M}_w$ 23 000) under the same conditions and worked up as above.

**Photolysis of 1 in the Presence of Methanol-$d_1$.** A solution of 0.458 g (2.08 mmol) of **1** and 2.5 mL of methanol-$d_1$ in ca. 100 mL of dry benzene was irradiated with a 10-W low-pressure mercury lamp at room temperature for 12.5 h. The solvent benzene and the remaining methanol-$d_1$ were evaporated, and the residue (0.55 g) was chromatographed by using a 1.8 × 25 cm silica gel column which had been packed in hexane. The column was eluted with a 3:2 mixture of hexane and benzene to give 30 mg (5 wt %, $\bar{M}_w$ 1000) of the product and then eluted with THF to give 0.456 g (83 wt %, $\bar{M}_w$ 1400) of the product: $\bar{M}_w$ 1000; $^1$H NMR $\delta$ 0.51–0.70 (m, MeSi), 1.03–1.42 (m, EtSi), 3.52 (s, CH$_3$O), 4.73 (m, HSi), 7.65 (br s, ring protons).

**Photolyses of 2 in Solutions.** A benzene solution (25 mL) containing 0.1521 g of **2** ($\bar{M}_w$ 18 500) was irradiated with a 6-W low-pressure mercury lamp for 2 h at room temperature. The solvent benzene was evaporated, and the residue was heated at 70–80 °C in vacuo to give 0.1573 g of the photoproducts: $\bar{M}_w$ 5800; IR 2110 cm$^{-1}$; $^1$H NMR $\delta$ 0.43 (br m, MeSi), 4.85 (m, HSi), 6.6–7.6 (m, phenyl and phenylene ring protons). Each 25 mL of the above solution was photolyzed for a definite time to obtain a relationship between molecular weights and irradiation time (see Figure 2). The photolyses of **2** in the presence of methanol were carried out by using a mixture of 25 mL of the above benzene solution and 0.2 mL of methanol. The following is typical of the procedures used. A mixture of 25 mL of a solution containing 0.1521 g of **2** and 0.2 mL of methanol was irradiated for 6 h under the same conditions. The solvent benzene and methanol were evaporated, and the residue was heated at 70–80 °C in vacuo for 1 h to give 0.1564 g of the photoproducts: $\bar{M}_w$ 2000; IR 2120, 1090 cm$^{-1}$; $^1$H NMR $\delta$ 0.58 (br m, MeSi), 3.4 (br s, MeO), 5.3 (m, HSi), 6.7–6.9 (m, phenyl and phenylene ring protons).

**Isolation of the Photoproducts from 2 in the Presence of Methanol-$d_1$.** A solution of 0.5685 g (1.8 mmol) of **2** and 2.0 mL of methanol-$d_1$ in 100 mL of dry benzene was irradiated with a 10-W low-pressure mercury lamp at room temperature for 4 h. The solvent benzene and the remaining methanol-$d_1$ were evaporated, and the residue (0.5844 g) was chromatographed by using a 2 × 15 cm silica gel column which had been packed in hexane. The column was eluted with a 1:1 mixture of benzene and hexane to give 32.7 mg (6% yield) of 1,4-bis(methylphenylsilyl)benzene and 90.3 mg (15 wt %) of fraction 2. Then the column was eluted with THF to give 0.4552 g (78% wt%) of fraction 3. For 1,4-bis(methylphenylsilyl)benzene: IR 2110 cm$^{-1}$; $^1$H NMR $\delta$ 0.63 (d, 6 H, MeSi, $J = 4$ Hz), 4.88 (q, 2 H, HSi, $J = 4$ Hz), 7.1–7.7 (m, 14 H, phenyl and phenylene ring protons); exact mass calcd for $C_{20}H_{22}Si_2$ 318.1260, found 318.1247. For fraction 2: $\bar{M}_w$ 1000; $^1$H NMR $\delta$ 0.2–0.8 (m, MeSi), 3.50 (m, MeO), 4.4 (m, HSi), 7.0–7.7 (m, phenyl and phenylene ring protons); decoupled $^{13}$C NMR $\delta$ −5.14, −3.89 (t, $J = 18.3$ Hz), −3.61, −3.45, −1.28, −0.60 (CH$_3$Si and DCH$_2$Si), 51.27 (CH$_3$O), 127.71, 127.84, 127.90, 127.93, 129.40, 129.55, 129.78, 129.89, 133.15, 133.29, 133.32, 133.34, 133.49, 133.56, 133.58, 133.69, 133.79, 133.92, 133.97, 134.02, 134.10, 134.17, 134.20, 134.32, 134.45, 134.53, 134.60, 134.64, 134.65, 134.84, 135.09, 135.18, 135.27, 135.52 (ring carbons). For fraction 3: $\bar{M}_w$ 2500; $^1$H NMR $\delta$ 0.6 (br m, MeSi), 3.5 (br m, MeO), 4.9 (m, HSi), 6.9–7.7 (m, phenyl and phenylene ring protons).

**Photolyses in Solid Films.** The polymers **1** ($\bar{M}_w$ 34 000) and **2** ($\bar{M}_w$ 27 500) were used for the photolyses in the solid films. The following is typical of the procedures used. A toluene solution of the polymer **1** (5 wt %) was spin-coated on a quartz plate by spinner (5000 rpm). The film was baked at 120 °C for 30 min. The thickness of the resulting film was measured to be 0.1 μm. The film thus obtained was irradiated with a 500-W Xe–Hg lamp for 30 s in the air. The UV spectra of the films, before and after irradiation, are shown in Figure 4 for **1** and in Figure 6 for **2**. The films for IR spectra (ca. 0.5 μm thick) were prepared on a KBr plate by spin coating (1000 rpm) of a 5% toluene solution of the

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polymers, prebaked at 120 °C, and then irradiated with a 500-W Xe–Hg lamp for 2 min.

**Registry No.** 1 (homopolymer), 95014-59-8; 2 (homopolymer), 95014-60-1; 4-EtOEtMeSiC$_6$H$_4$SiMeEtOEt, 95736-24-6; (EtO)$_2$SiEtMe, 18294-09-2; 4-BrC$_6$H$_4$Br, 106-37-6; 4-EtMeClSiC$_6$H$_4$SiClMeEt, 95014-58-7; 4-EtOMePhSiC$_6$H$_4$SiPhMeOEt, 16165-75-6; 4-(EtO)$_2$MeSiPh, 775-56-4; 4-BrMgC$_6$H$_4$MgBr, 2425-81-2; 4-MePhClSiC$_6$H$_4$SiClPhMe, 18666-79-0.

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# Stoichiometry of Diorganotin Dihalide Adducts in Solution

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The formation of Lewis acid–base adducts of diorganotin dihalides of the type R$_2$SnX$_2$, where R = CH$_3$, C$_2$H$_5$, C$_3$H$_7$, *n*-C$_4$H$_9$, *t*-C$_4$H$_9$, or C$_6$H$_5$ and X = Cl or Br, with a variety of bases (triphenylphosphine oxide [TPPO], Me$_2$SO, DMA, diphenyl sulfoxide, dibenzyl sulfoxide, pyridine *N*-oxide, and acetonitrile) was studied by both NMR spectroscopy and calorimetry. The $^{31}$P chemical shift of TPPO and the $^{119}$Sn shift of the acid were monitored as a function of concentration. The effects of different equilibria including formation of the 1:1 adduct, the 1:2 adduct, simultaneous formation of the 1:1 and 1:2 adducts, and simultaneous formation of the 1:1 adduct and either associated acid, associated base, or associated adduct on the NMR shifts as a function of concentration were determined by computer simulation. The experimentally observed plots can be attributed to predominant formation of the 1:1 adduct along with the associated adduct. The formation of the 1:2 adduct also occurs in solution as demonstrated by isolation of 1:2 adducts and the curvature obtained in the chemical shift plots for weak acids and bases. Calorimetric data were analyzed by schematic mapping and show that the only model that successfully reproduces the data is predominant formaton of the 1:1 adduct. The size of the substituents on the acid was found to have a significant effect on the equilibrium constants; the constants for di-*tert*-butyltin dichloride were a factor of 100 lower than those of dimethyltin dichloride. Base strengths toward dimethyltin dichloride vary in the order TPPO > pyridine *N*-oxide > Me$_2$SO ≥ DMA ≥ dibenzyl sulfoxide ≥ diphenyl sulfoxide > acetonitrile. Previous reports that the 1:2 adducts are favored for the dihalotins are most likely a result of the use of excess base to precipitate the 1:2 adduct and the generally greater insolubility of the 1:2 adduct.

## Introduction

Organotin halides comprise one of the most convenient systems for the investigation of Lewis acid–base interactions. The acids are stable and not extremely sensitive to moisture and have no lone pair electrons on the central atom. Moreover, the heats of interaction are in a range accessible for study by calorimetry, there are two spin $^1/_2$ isotopes of moderate abundance that provide coupling constant and chemical shift data, and the nucleus can also be studied by Mössbauer spectroscopy. In the majority of the studies of complexation of these acids, the complexes have been isolated in the solid state and then studied by a variety of techniques such as IR, NMR, and, occasionally, X-ray diffraction. The results of these studies indicate that with monodendate bases the triorganotin halides form 1:1 complexes with trigonal-bipyramidal geometry, and the diorganotin dihalides and organotin trihalides form 1:2 complexes with octahedral geometry. Most studies of the complexes in solution have reported the same stoichiometries.[1,2]

That the triorganotin halides form 1:1 complexes in solution and in the solid state has been firmly established, but there is a small body of literature that suggests that 1:1 stoichiometry is also favored for the diorganotin dihalides and possibly even the trihalides in solution. Both 1:1 and 1:2 complexes of (CH$_3$)$_2$SnCl$_2$ with DMF,[3] 1:1 complexes of (CH$_3$)$_2$SnCl$_2$ with aromatic carbonyls,[3] 1:1 and 1:2 complexes of (CH$_3$)$_2$SnCl$_2$ with alkyl sulfoxides (but only 1:1 for dibenzyl sulfoxide),[4,5] only 1:1 complexes for (CH$_3$)$_2$SnCl$_2$ and (C$_6$H$_5$)$_2$SnCl$_2$ with tribulylphosphine,[6] and both 1:1 and 1:2 complexes of (CH$_3$)$_2$SnCl$_2$ and (CH$_3$)$_2$SnBr$_2$ with Me$_2$SO, DMF, and HMPT[7] have been reported. Recently, Fujiwara, Sakai, and Sasaki have used NMR to determine equilibrium constants for the reaction of (CH$_3$)$_2$SnCl$_2$ with Me$_2$SO, DMF, HMPT,[8] pyridine,[9] and picolines[10] in solution and have found that the 1:1 complex is favored in all cases.

As part of our continuing investigation[11,12] of the Lewis acidities of the organometallic group 14 halides, we report

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