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LASER-PHOTOLYSIS STUDY OF ARYL-SUBSTITUTED SILYL AND STANNYL ANIONS

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Photochemical primary processes of aryl-substituted silyl and stannyl anions were studied at room temperature. The silyl and stannyl radicals generated were observed directly by laser-photolysis.

Metalloidal anions, especially of silyl and stannyl anions, are useful for synthetic chemistry and reaction mechanism.1-5) Although extensive thermal reactions of silyl and stannyl anions have been made, there are few reports on photochemical studies of these anions.6-8) Recently, Ito, Aruga, and Matsuda7,8) have reported that important reaction intermediates generated by photolysis of triphenylsilyl and triphenylstannyl anions are the corresponding silyl and stannyl radicals, respectively, by the electron-trapping technique of aromatic compounds. The direct identification of reaction intermediates generated by photolysis of silyl and stannyl anions is key problem to clarify the reaction mechanism. In this communication, we describe the direct observation of aryl-substituted silyl and stannyl radicals by photoejection of the corresponding silyl and stannyl anions ($Ph_nMe_{3-n}ELi$, **1**-**3** for E=Si and n=1-3, and **4** for E=Sn and n=3, respectively) by laser-photolysis at room temperature.

The syntheses of **1**-**4** in tetrahydrofuran (THF) were carried out as described in literature.1) Compounds **1**-**4** were identified by absorption bands (all 355 nm for **1**-**3** and 310 nm for **4**, respectively) and ^1H and ^{13}C NMR spectra.7,9,10) The THF solution containing **1** or **4** in a Pyrex tube was degassed and then irradiated at room temperature by a Xenon lamp for 10 min. The reaction products were analyzed with a gas chromatograph and liquid chromatograph.

Laser-photolysis measurements were performed on the degassed solutions at room temperature by using the fourth harmonic pulse (266 nm and 5 ns width) of a Quanta-Ray DCR-1 Nd:YAG laser as the exciting light source. The laser-photolysis apparatus and measuring system were similar to those published elsewhere.11)

The time dependence of absorbance of the transient absorption, A(t), was measured with each of the THF solutions of **1**-**4**. The time resolved absorption spectra of **1**-**4** observed at 200 ns after excitation are shown in Fig. 1. Signals were obtained below 350 nm for all the solutions containing **1**-**4** as shown in Fig. 1. From the plots of 1/A(t) against t for **1**-**4**, the early stages of the A(t) curves observed with these compounds were proved to decay with second order kinetics. As typical examples, the plots of 1/A(t) against t for **1** and **4** were shown in Fig. 2. The $k/\varepsilon\ell$ values were obtained to be 0.38 (at 315 nm), 0.34 (at 320 nm), 0.42 (at 320 nm), and 7.7 (at 330 nm) x $10^7\ s^{-1}$ for **1**, **2**, **3**, and **4**, respectively. Here k is the rate constant of the second order decay, ε is the molar extinction coefficient, ℓ is the optical length of the apparatus employed (about 5 mm).

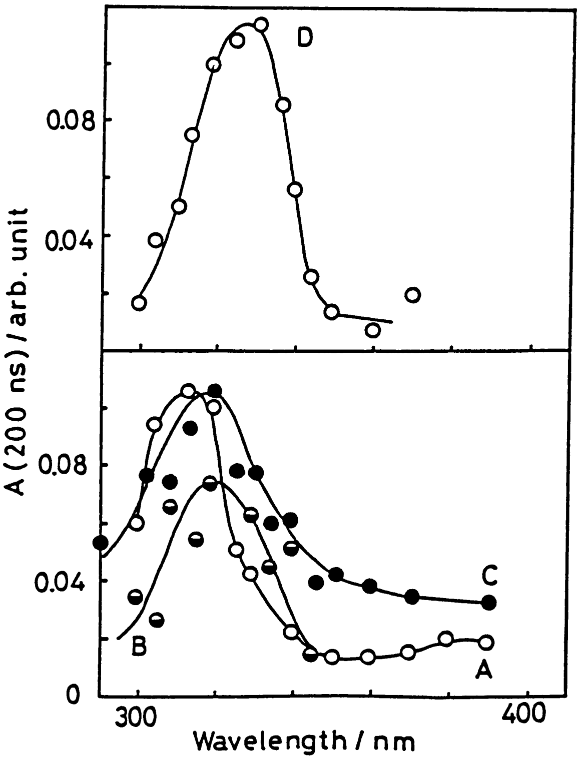
Spectra A, B, C, and D can safely be assigned to the aryl-substituted silyl and stannyl radicals ($Ph_nMe_{3-n}E\cdot$, E=Si and n=1-3, E=Sn and n=3, respectively) generated by the direct photoejection from **1**-**4**.

$$Ph_nMe_{3-n}E^- \xrightarrow{h\nu} Ph_nMe_{3-n}E\cdot + e^-_{solv} \qquad (1)$$

E=Si, n=1-3
E=Sn, n=3

This assignment can be derived from the following reasons: (1) The spectra shapes and peak positions (320 nm and 330 nm) of Spectra C and D, respectively, agree well with those reported for $Ph_3Si\cdot$ and $Ph_3Sn\cdot$.12) No spectra of $PhMe_2Si\cdot$ and $Ph_2MeSi\cdot$ have been reported. However, the spectral shapes and positions (315 nm and 320 nm) of Spectra A and B resemble those for $PhH_2Si\cdot$ and $Ph_2HSi\cdot$.12) (2) Upon irradiation of the THF solutions containing **1** and **4** with a Xenon lamp for 10 min., disilane and distannane for **1** and **4** were obtained. The disilane and distannane are considered to be derived from the silyl and stannyl radicals generated by the direct photoejection from **1** and **4**, respectively.

$$2\ Ph_nMe_{3-n}E\cdot \longrightarrow (Ph_nMe_{3-n}E)_2 \qquad (2)$$



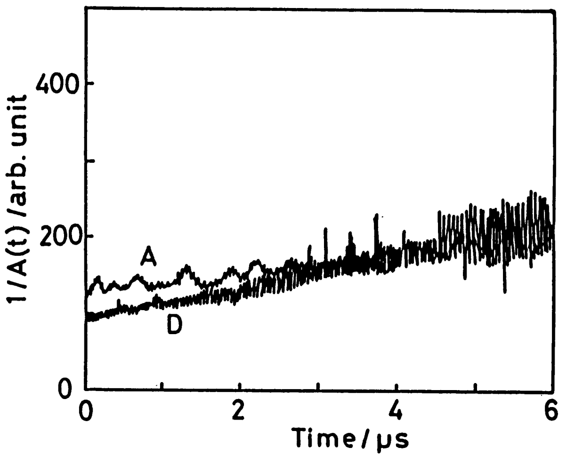


Fig. 2. Plots of 1/A(t) against t observed with the THF solutions of (A) **1** (at 315 nm) and (D) **4** (at 330 nm), respectively.

Fig. 1. Transient absorption spectra observed 200 ns after excitation of the THF solutions containing (A) **1**, (B) **2**, (C) **3**, and (D) **4**, respectively. The concentrations of **1**-**4** are ca. 2.0-3.0 x 10^{-3} mol dm^{-3}.

No absorption band for a solvated electron (e^{-}_{solv}) in THF could be observed in the visible region using our apparatus.

To the best of our knowledge, this is the first dintinct observation of aryl-substituted silyl and stannyl radicals generated by the direct photoejection of the corresponding silyl and stannyl anions.

The photoejection of the stannyl anions occurred easily compared with that of the silyl anions. The deriving force for such photoejection process may be considered to be dependent on the oxidation potentials of these anions.13) In fact, the oxidation potential of triphenylstannyl anion is lower than that of the corresponding silyl anions.14)

In this study, we first carried out laser-photolysis studies of aryl-substituted silyl and stannyl anions and observed directly the generated silyl and stannyl radicals by photoejection. The present study will give useful information on photochemistry and synthetic chemistry of organometallic compounds.

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