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LASER-PHOTOLYSIS STUDY OF ARYL-SUBSTITUTED GERMYL ANIONS

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

Among the key problems in photochemical reactions of organic anions and metalloidal anions, especially of the group 4B elements, is the identification of labile intermediates formed during reaction. The laser-photolysis technique is a good method for direct observation of transient species generated immediately after excitation for the anions. Although extensive photochemical studies of organic anions have been made,[1)] there are few reports on group 4B element-centered anions.[2-4)] Particularly no report on germyl anions has appeared. The present report describes the studies of photochemical reactions of aryl-substituted germyl anions ($Ph_nMe_{3-n}GeLi$, **1**-**3** for n=1-3, respectively) at room temperature.

The syntheses of **1**-**3** in tetrahydrofuran (THF) were carried out as described in literature.[5)] Compounds **1**-**3** were identified by the absorption bands (290 nm, 310 nm, and 310 nm for n=1, 2, and 3, respectively) and ^1H and ^{13}C NMR spectra. 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.[6)]

Laser-photolysis of the solutions containing **1**-**3** yielded transient absorption spectra as shown in Fig. 1. Signals were obtained below 350 nm for all the solutions containing **1**-**3** as shown in Fig. 1. The signals of **1**-**3** (Spectra A, B, and C of Fig. 1) were found to decay with second order kinetics. The k/ε values were obtained to be ca. 2.8 (at 320 nm), ca. 3.2 (at 330 nm), and ca. 4.8 (at 320 nm) x $10^7\ s^{-1}cm$ for **1**, **2**, and **3**, respectively. Here k is the rate constant of the second order decay and ε is the molar extinction coefficient. Neither the absolute nor the relative value of k can be obtained because no information about ε has been given for the germyl radicals.

Spectra A, B, and C can be safely be assigned to the aryl-substituted germyl radicals ($Ph_nMe_{3-n}Ge\cdot$) generated by direct photoejection from **1**-**3**.

$$Ph_nMe_{3-n}Ge^- \xrightarrow{h\nu} Ph_nMe_{3-n}Ge\cdot \quad + \quad e^-_{solv}$$

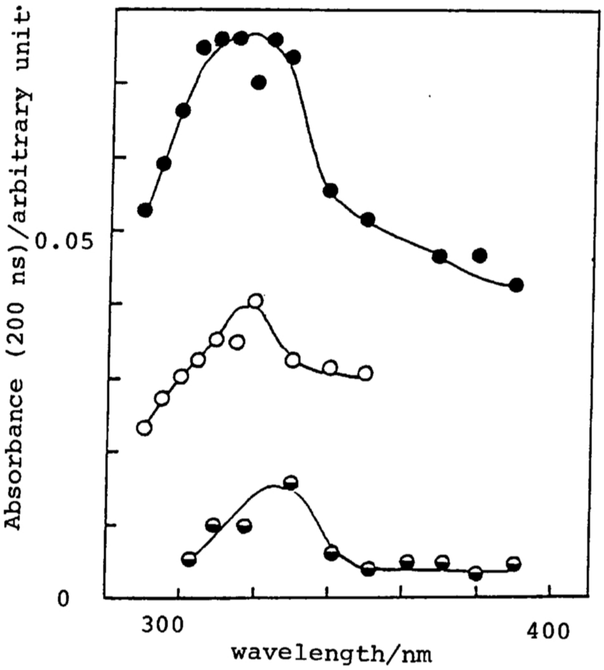

Fig. 1. Transient absorption spectra observed after excitation of the THF solutions containing (A) **1**, (B) **2**, and (C) **3**, respectively. Each concentrations of **1**-**3** is ca. 2.0-3.0 x 10^{-3} mol dm^{-3}.

This assignment can be derived from the following reasons: (1) The spectral shapes and peak positions (315 nm, 330 nm, and 330 nm) of Spectra A, B, and C, respectively, agree well with those generated by abstraction of hydrogen of the aryl-substituted germanes ($Ph_nMe_{3-n}GeH$) with t-butoxyl radical.7,8) (2) Upon irradiation of the THF solutions containing **1**-**3** with a Xenon lamp for 1 h, digermanes were obtained in high yields. The digermanes are considered to be derived from the aryl-substituted germyl radicals generated by the direct photoejection from **1**-**3**. No absorption band for a solvated electron (e^-_{solv}) was observed in the visible region.

So far as we are aware, this work represents the first observation of the neutral radicals generated by the direct photoejection of the group 4B element-centered anions by laser-photolysis.

Further laser-photolysis studies on germyl anions and related compounds are now in progress.

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