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DIRECT OBSERVATION OF GERMYL RADICALS BY A LASER-PHOTOLYSIS OF GERMYL KETONES

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Photochemical primary processes of benzoyltriphenylgermane and benzoylphenyldimethylgermane were studied at room temperature in cyclohexane and chloroform. The germyl radicals generated were observed directly with the aid of a laser-photolysis technique.

Photochemical reactions of metalloidal ketones have received considerable attention in connection with the stereochemistry and chemical reactivity of organometallic radicals.[1] Although the photochemistry of some bis(metalloidal)ketones ($(RM)_2CO$)[1-3] and some acylsilanes (XSiCOY)[1-3] has been hitherto investigated, that of any acylgermanes (XGeCOY) has not been studied yet. This communication reports preliminary results of the studies of photochemical reactions of benzoyltriphenylgermane ($Ph_3GeCOPh$, 1) and benzoylphenyldimethylgermane ($PhMe_2GeCOPh$, 2) in solution at room temperature. The reaction of benzoylphenyldimethylsilane (3) was also studied as a reference compound.

Photochemical reactions of silyl ketones have been considered to proceed via Norrish type 1 cleavage, siloxycarbene, or formation of silaethene dependent upon the structure of the silyl ketones and the reaction conditions employed.[3] Although many reaction intermediates in photochemical reactions of organic ketones have observed with the aid of laser-photolysis techniques,[4] the photochemical reactions of metalloidal ketones has not been studied directly by a laser-photolysis technique. We have carried out a laser-photolysis study of 1-3 and observed, for the first time, the transient absorptions due to the reaction intermediates generated immediately after excitation of metalloidal ketones.

The syntheses of 1[5] and 3[6] were carried out as described in literatures. We newly synthesized 2[7] by the method of Yamamoto et al.[6] The cyclohexane solution containing 2 or 3 (0.2 mol dm^{-3}) in Pyrex tubes was degassed and then irradiated at room temperature by a high-pressure mercury lamp for 1 h. The reaction products were analyzed with a gas chromatograph.

Laser-photolyis 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.[4] Spectro-

grade cyclohexane and chloroform were used for the solvents.

The time dependence of absorbance of the transient absorption, A(t), was measured for 1-3 in cyclohexane solution. The time resolved absorption spectra observed immediately after the excitation of the solutions were obtained from A (0 ns) values at various wavelengths and are shown in Fig. 1. Here, we took the excitation time by the laser-pulse as the initial time (t=0 ns).

Strong signals were obtained below 350 nm for all the solutions as shown in Fig. 1. The signal of 3 (Spectrum C of Fig. 1) decayed very fast. Its lifetime was shorter than the time resolution (about 20 ns) of the present apparatus. On the other hand, the signals of 1 and 2 (Spectra A and B of Fig. 1) were found to decay more slowly. The plots of 1/A(t) against t for 1 and 2 were shown in Fig. 2. From these plots, the early stages of the A(t) curves observed with these compounds were proved to decay with second order kinetics. The $k/\varepsilon\ell$ values were obtained to be 0.58 (at 325 nm) and 2.6 (at 315 nm) x 10^6 s^{-1} for 1 and 2, 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 and B can safely be assigned to the germyl radicals ($Ph_3Ge\cdot$ for 1 and $PhMe_2Ge\cdot$ for 2) generated from the following reactions:

$$XGeCOPh \xrightarrow{h\nu} {}^{*}XGeCOPh \qquad (1)$$

$${}^{*}XGeCOPh \longrightarrow XGe\cdot + \cdot COPh \qquad (2)$$

This assignment can be derived from the following reasons: (1) The spectral shapes and peak positions (330 nm and 315 nm) of Spectra A and B, respectively, agree well with those reported for $Ph_3Ge\cdot$.[8,9] and $PhMe_2Ge\cdot$.[10] (2) Upon irradiation of the cyclohexane solution containing 2 with a mercury lamp for 1 h, diphenyltetramethyldigermane was obtained.[11] The digermane is considered to be derived from the germyl radical ($PhMe_2Ge\cdot$). This fact can be explained well the following reaction:

$$2\ XGe\cdot \longrightarrow XGe\text{-}GeX \qquad (3)$$

To the best our knowledge, this is the first observation of organogermyl radicals in the reactions of germyl ketones with the aid of laser-photolysis techniques. Although the $k/\varepsilon\ell$ values were measured for $Ph_3Ge\cdot$ and $PhMe_2Ge\cdot$ in cyclohexane in this study, neither the absolute nor the relative value of k can not be obtained because no information about ε has not been given for the germyl radicals.

The peak position of Spectrum C could not be measured, but its spectral shape resembles that for $PhH_2Si\cdot$.[9] However, Spectrum C may be due to the lowest singlet state (S_1) of 3 because the cyclohexane solution of 3 was found to be almost unchanged upon irradiation by a mercury lamp for 1 h.[12] Since the lowest peak (444 nm) of its n,π^* absorption band was observed to lie much lower than that (294 nm) of the π,π^* band, the S_1 lifetime of 3 is considered to be increased very much

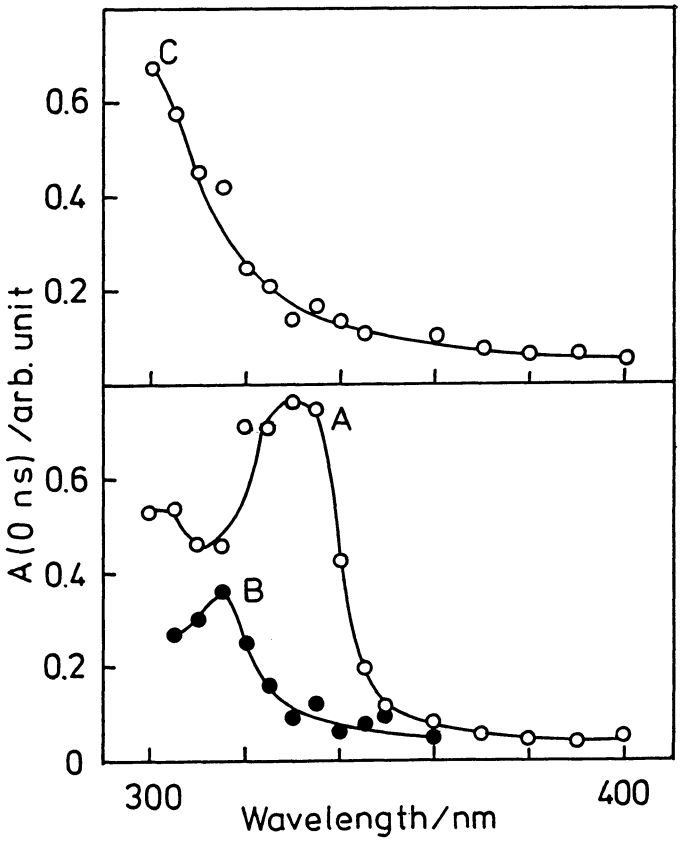

Fig. 1. Transient absorption spectra observed immediately after excitation of the cyclohexane solutions containing (A) 1, 1.23 x 10^{-3} mol dm^{-3}, (B) 2, 3.77 x 10^{-3} mol dm^{-3}, (C) 3, 1.91 x 10^{-3} mol dm^{-3}, respectively.

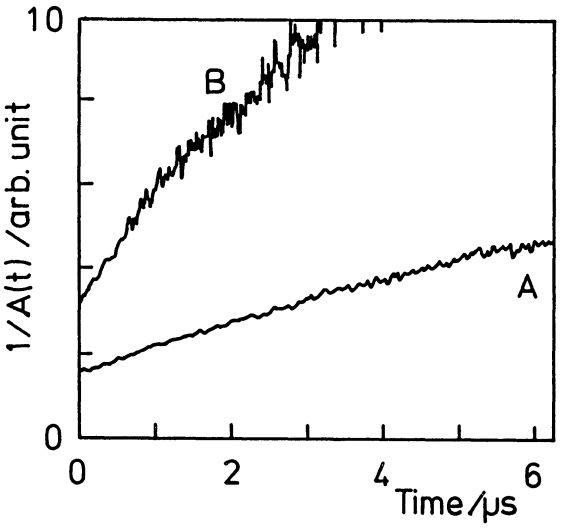

Fig. 2. Plots of 1/A(t) against t observed with the cyclohexane solutions of (A) 1 and (B) 2, respectively.

from the corresponding organic ketones where the S_1 lifetime are very short (less than 1 ns) due to very small splitting between their lowest n,π^* and π,π^* states. Since the lowest n,π^* states of 1 and 2 (about 440 nm) were also found to be much lower than the lowest π,π^* ones (about 295 nm), the Norrish type 1 cleavage is considered to proceed through S_1 for 1 and 2.

Similar transient absorption spectra as Spectra A-C of Fig. 1 were obtained upon excitation of 1-3 in chloroform by the laser pulse, respectively. The A(t) curves observed for 1 and 2 in chloroform decayed much faster than the corresponding A(t) curves observed in cyclohexane. This may be due to the fast trapping of the generated germyl radicals by chloroform. Indeed, the trapping rate constant of $Ph_3Ge\cdot$ by chloroform was estimated to be 7.2 x 10^6 s^{-1} in cyclohexane.[8)]

The lifetime of the signal observed for 3 in chloroform was also shorter than the time resolution of the present apparatus. This might be due to an exciplex formation of its S_1 with chloroform as proposed by Porter and Iloff.[14)] However, in the following reactions after the exciplex formation, no transient absorption due to any reaction intermediate could be observed.

In this study, we first carried out a laser-photolysis study of germyl ketones and observed directly the generated germyl radicals. Direct measurements using laser-photolysis techniques will further give direct informations on photochemical processes of metalloidal ketones.

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