CHEMISTRY LETTERS, pp. 513-514, 1986.

CIDEP STUDY OF THE FORMATION OF ARYL-SUBSTITUTED GERMYL RADICALS IN DIRECT PHOTOEJECTION OF THE GERMYL ANIONS

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Photolysis of aryl-substituted germyl anions was studied by CIDEP at 77 K. The emmision pattern of the spectra detected after pulsed excitation revealed a contribution of the triplet mechanism.

The photoejection process from organic anions and metalloidal anions, especially of the group 4B elements, has received considerable interest in relation to the intermediates of photostimulated $S_{RN}1$ reactions.[1-7] We previuosly reported the first observation of aryl-substituted germyl radicals generated by the direct photoejection of the corresponding germyl anions by laser-photolysis at room temperature.[8] In order to clarify the mechanism of this photoejection process, we carried out a chemically induced dynamic electron polarization (CIDEP) study of the photochemical reactions of aryl-substituted germyl anions ($Ph_nMe_{3-n}GeLi$, **1**-**3** for n=1-3, respectively) at 77 K.

The syntheses and identification of **1**-**3** have been described previously.[8] CIDEP measurements were performed on the degassed solutions at 77 K by using a Molectron UV 24 nitrogen gas laser (337.1 nm) as the exciting light source. The CIDEP apparatus and measuring system were similar to those published elsewhere.[9]

Each CIDEP spectrum, observed at an early stage (time delay of 1.2 μs after excitation), of the THF solutions containing **1**-**3** at 77 K had a broad emmisive pattern with a large g factor. No signals were observed at room temperature. As a typical example, Figure 1 shows the CIDEP spectrum of **2**. The g factors for **1**-**3** are given in Table 1.

The signals can safely be assigned to the aryl-substituted germyl radicals. This assignment can be derived from the following reasons: (1) The aryl-substituted germyl radicals generated by the direct photoejection of **1**-**3** by laser-photolysis at room temperature were detected.[8] (2) The g factors obtained are large and change significantly depending on their substituents, and agree well those reported for $Ph_nMe_{3-n}Ge\cdot$.[10]

The emmisive phase patterns observed for **1**-**3** are due to the triplet mechanism (TM).[11] Thus, the following primary processes for the formation of aryl-substi-

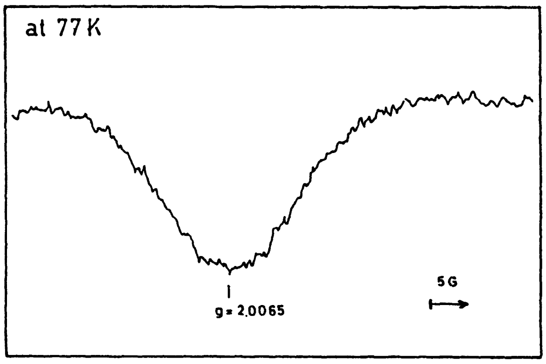

Fig. 1. The CIDEP spectrum of 2 at a time delay of 1.2 μs after the laser excitation.

Table 1. The g Factors of Signals Generated by the Photoejection of 1-3

Compound	g factor[a)]	reference
$PhMe_2GeLi$ (1)	2.0088	this work
	2.0086	[10]
$Ph_2MeGeLi$ (2)	2.0065	this work
	2.0070	[10]
Ph_3GeLi (3)	2.0055	this work
	2.0054	[10]

a) The g factors were determined by reference to that of the biphenyl anion radical.

tuted germyl radicals generated by the direct photoejection of the germyl anions are proposed.

$$Ph_nMe_{3-n}Ge^- \xrightarrow{h\nu} {}^1(Ph_nMe_{3-n}Ge^-)^* \qquad (1)$$

$$ {}^1(Ph_nMe_{3-n}Ge^-)^* \longrightarrow {}^3(Ph_nMe_{3-n}Ge^-)^* \qquad (2)$$

$$ {}^3(Ph_nMe_{3-n}Ge^-)^* \longrightarrow Ph_nMe_{3-n}Ge\cdot \; + \; e^- \qquad (3)$$

No CIDEP signal of electron in Eq. 3 was observed. The absence of electron signal may be most probably explained by the fact that the electron generated by photoejecton of 1-3 in Eq. 3 is trapped by lithium cation to give lithium metal.

Further CIDEP studies on germyl anions and related compounds are now in progress.

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(Received January 17, 1986)