

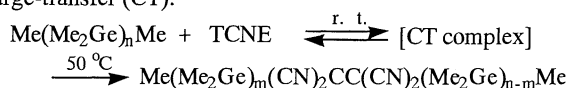
## Tetracyanoethylene-induced Chlorinative Cleavage of Permethylated Oligogermanes with Polyhalomethanes

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In the presence of tetracyanoethylene (TCNE), Ge-Ge bonds of oligogermanes (Me(Me<sub>2</sub>Ge)<sub>n</sub>Me, n=2-5) were cleaved with CCl<sub>4</sub> to yield the corresponding chlorogermanes. A mechanism involving an oligogermane radical cation is proposed for the Ge-Ge cleavage.

Recently, we have described the first insertion reaction of TCNE into oligogermanes (Me(Me<sub>2</sub>Ge)<sub>n</sub>Me) via electron transfer (ET).<sup>1</sup> In this reaction, TCNE insertion into oligogermanes depends on the nature of oligogermane cation radicals generated by charge-transfer (CT).



In the course of our studies on an electron transfer reaction of oligogermanes, we found new chlorinative cleavage of the Ge-Ge bonds of oligogermane via cation radicals. Si-Si bonds of oligosilanes undergo chlorinative cleavage on irradiation in CCl<sub>4</sub>-CH<sub>2</sub>Cl<sub>2</sub> containing dicyanoanthracene.<sup>2</sup>

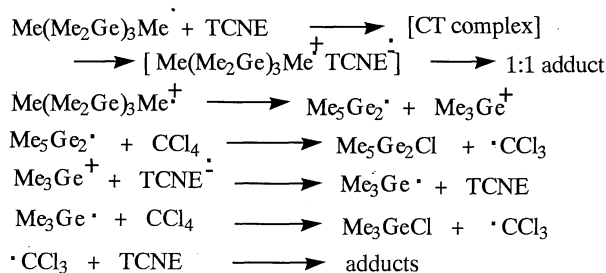
A mixture of octamethyltrigermane (Me(Me<sub>2</sub>Ge)<sub>3</sub>Me) and TCNE in CCl<sub>4</sub>-CH<sub>2</sub>Cl<sub>2</sub> solvents at 70 °C for 4 h gave trimethylchlorogermane (Me<sub>3</sub>GeCl, 28%), pentamethylchlorodigermane (Me<sub>5</sub>Ge<sub>2</sub>Cl, 32%), and hexachloroethane (trace), together with 1:1 adduct (15%).<sup>1</sup> The reaction did not occur without one equivalent of TCNE under the conditions. The 1:1 adduct formed was stable in CCl<sub>4</sub>. On mixed with other acceptors such as chloranil and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in CCl<sub>4</sub>-CH<sub>2</sub>Cl<sub>2</sub>, Me(Me<sub>2</sub>Ge)<sub>3</sub>Me also afforded Me<sub>3</sub>GeCl (4.4% and 6.0%) and Me<sub>5</sub>Ge<sub>2</sub>Cl (6.3% and 10%), respectively in rather poor yields. In the case of DDQ, most of Me(Me<sub>2</sub>Ge)<sub>3</sub>Me was converted to the 1:1 adduct (ca. 80%), but chloranil afforded only a trace amount of the 1:1 adduct with the trigermane. Even in a mixed solvent of CHCl<sub>3</sub>-CH<sub>2</sub>Cl<sub>2</sub>, the corresponding chlorogermane and chlorodigermane were formed but in lower yields.

In the presence of TCNE, the terminal Ge-Ge bonds and the internal Ge-Ge bonds of Me(Me<sub>2</sub>Ge)<sub>4</sub>Me and Me(Me<sub>2</sub>Ge)<sub>5</sub>Me were cleaved with CCl<sub>4</sub> to yield the corresponding chlorogermanes. The results are summarized in Table 1.

MINDO UHF calculation of Me(Me<sub>2</sub>Ge)<sub>3</sub>Me cation radical shows that the unpaired electron is nearly localized on the p orbital

of a Ge atom of Me<sub>5</sub>Ge<sub>2</sub> moiety, while the charge is localized in the Me<sub>3</sub>Ge moiety in the most stable configuration.

From these results, we propose the following scheme as one of possible reaction pathways.



Scheme 1.

At first, Me(Me<sub>2</sub>Ge)<sub>3</sub>Me is converted to the radical ion pair via a CT complex. Some parts of the radical ion may be transformed to the 1:1 adduct. On the other hand, Me(Me<sub>2</sub>Ge)<sub>3</sub>Me cation radical formed via CT undergoes spontaneous scission to Me<sub>5</sub>Ge<sub>2</sub><sup>·</sup> and Me<sub>3</sub>Ge<sup>+</sup>. The Me<sub>5</sub>Ge<sub>2</sub><sup>·</sup> abstracts a chlorine atom from CCl<sub>4</sub> to give the chlorodigermane and ·CCl<sub>3</sub>, while Me<sub>3</sub>Ge<sup>+</sup> is reduced by TCNE<sup>-·</sup> to afford Me<sub>3</sub>Ge<sup>·</sup> together with TCNE. The Me<sub>3</sub>Ge<sup>·</sup> thus formed abstracts a chlorine atom from CCl<sub>4</sub> to give Me<sub>3</sub>GeCl and ·CCl<sub>3</sub>. Finally, ·CCl<sub>3</sub> either adds to TCNE or dimerizes.

Table 1. TCNE-induced Chlorinative Ge-Ge Bond Cleavage of Oligogermanes with CCl<sub>4</sub>-CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>

Me(Me <sub>2</sub> Ge) <sub>n</sub> Me	Acceptor	Conv / %	Products(Yield, % <sup>b</sup> )
Me <sub>3</sub> GeGeMe <sub>3</sub>	TCNE	10	Me <sub>3</sub> GeCl (6.0)
Me(Me <sub>2</sub> Ge) <sub>3</sub> Me	TCNE	59	Me <sub>3</sub> GeCl (29), Me <sub>5</sub> Ge <sub>2</sub> Cl (32)
Me(Me <sub>2</sub> Ge) <sub>4</sub> Me	TCNE	100	Me <sub>3</sub> GeCl (22), Me <sub>5</sub> Ge <sub>2</sub> Cl (49) Me <sub>7</sub> Ge <sub>3</sub> Cl (18)
Me(Me <sub>2</sub> Ge) <sub>5</sub> Me	TCNE	100	Me <sub>3</sub> GeCl (15), Me <sub>5</sub> Ge <sub>2</sub> Cl (40) Me <sub>7</sub> Ge <sub>3</sub> Cl (35), Me <sub>9</sub> Ge <sub>4</sub> Cl <sup>c</sup>

a) Me(Me<sub>2</sub>Ge)<sub>n</sub>Me (0.05 mmol) / TCNE (0.2 mmol) / CCl<sub>4</sub> (3.0 mmol) / CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) at 70 °C for 4 h. b) Determined by GLC. c) Detected by GC-MS.

### References and Notes

- K. Mochida, C. Hodota, R. Hata, and S. Fukuzumi, *Organometallics*, **12**, 586 (1993).
- Y. Nakadaira, N. Komatsu, and H. Sakurai, *Chem. Lett.*, **1985**, 1781.