Tetracyanoethylene-induced Chlorinative Cleavage of Permethylated Oligogermanes with Polyhalomethanes

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In the presence of tetracyanoethylene (TCNE), Ge-Ge bonds of oligogermanes ($Me(Me_2Ge)_nMe$, n=2-5) were cleaved with CCl_4 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 ($Me(Me_2Ge)_nMe$) via electron transfer (ET).[1] In this reaction, TCNE insertion into oligogermanes depends on the nature of oligogermane cation radicals generated by charge-transfer (CT).

$$\mathrm{Me(Me_2Ge)_nMe + TCNE} \underset{}{\overset{\text{r. t.}}{\rightleftarrows}} \text{[CT complex]} \xrightarrow{50\ ^\circ\mathrm{C}} \mathrm{Me(Me_2Ge)_m(CN)_2CC(CN)_2(Me_2Ge)_{n-m}Me}$$

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_4-CH_2Cl_2 containing dicyanoanthracene.[2]

A mixture of octamethyltrigermane ($Me(Me_2Ge)_3Me$) and TCNE in CCl_4-CH_2Cl_2 solvents at 70 °C for 4 h gave trimethylchlorogermane (Me_3GeCl, 28%), pentamethylchlorodigermane (Me_5Ge_2Cl, 32%), and hexachloroethane (trace), together with 1:1 adduct (15%).[1] The reaction did not occur without one equivalent of TCNE under the conditions. The 1:1 adduct formed was stable in CCl_4. On mixed with other acceptors such as chloranil and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in CCl_4-CH_2Cl_2, $Me(Me_2Ge)_3Me$ also afforded Me_3GeCl (4.4% and 6.0 %) and Me_5Ge_2Cl (6.3% and 10%), respectively in rather poor yields. In the case of DDQ, most of $Me(Me_2Ge)_3Me$ 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 $CHCl_3$-CH_2Cl_2, 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 $Me(Me_2Ge)_4Me$ and $Me(Me_2Ge)_5Me$ were cleaved with CCl_4 to yield the corresponding chlorogermanes. The results are summarized in Table 1.

MINDO UHF calculation of $Me(Me_2Ge)_3Me$ cation radical shows that the unpaired electron is nearly localized on the p orbital of a Ge atom of Me_5Ge_2 moiety, while the charge is localized in the Me_3Ge moiety in the most stable configuration.

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

$$\begin{aligned}
&\mathrm{Me(Me_2Ge)_3Me + TCNE} \longrightarrow \text{[CT complex]} \\
&\quad \longrightarrow [\mathrm{Me(Me_2Ge)_3Me^{+\cdot}\ TCNE^{-\cdot}}] \longrightarrow \text{1:1 adduct} \\
&\mathrm{Me(Me_2Ge)_3Me^{+\cdot}} \longrightarrow \mathrm{Me_5Ge_2{\cdot} + Me_3Ge^{+}} \\
&\mathrm{Me_5Ge_2{\cdot} + CCl_4} \longrightarrow \mathrm{Me_5Ge_2Cl + {\cdot}CCl_3} \\
&\mathrm{Me_3Ge^{+} + TCNE^{-\cdot}} \longrightarrow \mathrm{Me_3Ge{\cdot} + TCNE} \\
&\mathrm{Me_3Ge{\cdot} + CCl_4} \longrightarrow \mathrm{Me_3GeCl + {\cdot}CCl_3} \\
&\mathrm{{\cdot}CCl_3 + TCNE} \longrightarrow \text{adducts}
\end{aligned}$$

Scheme 1.

At first, $Me(Me_2Ge)_3Me$ 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, $Me(Me_2Ge)_3Me$ cation radical formed via CT undergoes spontaneous scission to $Me_5Ge_2\cdot$ and Me_3Ge^+. The $Me_5Ge_2\cdot$ abstracts a chlorine atom from CCl_4 to give the chlorodigermane and $\cdot CCl_3$, while Me_3Ge^+ is reduced by $TCNE^{-\cdot}$ to afford $Me_3Ge\cdot$ together with TCNE. The $Me_3Ge\cdot$ thus formed abstracts a chlorine atom from CCl_4 to give Me_3GeCl and $\cdot CCl_3$. Finally, $\cdot CCl_3$ either adds to TCNE or dimerizes.

Table 1. TCNE-induced Chlorinative Ge-Ge Bond Cleavage of Oligogermanes with CCl_4-CH_2Cl_2 [a]

$Me(Me_2Ge)_nMe$	Acceptor	Conv / %	Products(Yield,% [b])
$Me_3GeGeMe_3$	TCNE	10	Me_3GeCl (6.0)
$Me(Me_2Ge)_3Me$	TCNE	59	Me_3GeCl (29), Me_5Ge_2Cl (32)
$Me(Me_2Ge)_4Me$	TCNE	100	Me_3GeCl (22), Me_5Ge_2Cl (49) Me_7Ge_3Cl (18)
$Me(Me_2Ge)_5Me$	TCNE	100	Me_3GeCl (15), Me_5Ge_2Cl (40) Me_7Ge_3Cl (35), Me_9Ge_4Cl [c]

a) $Me(Me_2Ge)_nMe$ (0.05 mmol) / TCNE (0.2 mmol) / CCl_4 (3.0 mmol) / CH_2Cl_2 (5 cm^3) at 70 °C for 4 h. b) Determined by GLC. c) Detected by GC-MS.

References and Notes

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