Cleavage of Tin-Carbon Bonds of Organosilylstannane and Organodistannane in Photo-Induced Electron Transfer Reactions and Mass Spectrometry

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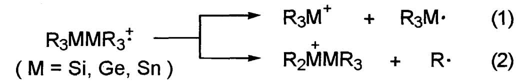
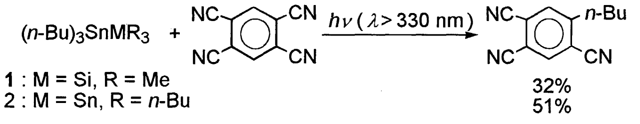
(Received September 28, 1994)

Photoalkylation of tetracyanobenzene and benzil with $(n\text{-Bu})_3\text{SnSiMe}_3$ or $(n\text{-Bu})_3\text{SnSn}(n\text{-Bu})_3$ proceeds *via* electron transfer. In these reactions, the Sn–C bond of $(n\text{-Bu})_3\text{SnSiMe}_3$ and $(n\text{-Bu})_3\text{SnSn}(n\text{-Bu})_3$ is cleaved in preference to the Sn–Si and Sn–Sn bonds. Similar cleavage of the Sn–C bond is also observed in mass spectra of these group 14 organometallic compounds.

Catenated group 14 organometallic compounds have been well known as effective σ-electron donors. The metal–metal bonds of these compounds, including organopolysilanes,[1] -germanes,[2] -stannanes,[3] and so on,[4] have been reported to be cleaved in the presence of electron acceptors *via* electron transfer (pathway 1). Recently, we have reported photo-induced electron transfer reactions of hexamethyldisilane with aromatic nitriles, in which the Si–Si bond of hexamethyldisilane is cleaved and the trimethylsilyl group is introduced to the aromatic nitriles.[1d] In the course of the investigation, we attempted to conduct the photo-induced electron transfer reactions using heavier group 14 organometals with more electron-donating ability. When bimetallic organotin compounds were used, the Sn–C bond was unexpectedly cleaved (pathway 2), and the alkyl group was introduced to the aromatic nitrile.[5] We report herein novel cleavage of the Sn–C bond in the photoalkylation of tetracyanobenzene and benzil[6] using the organotin compounds and the analogous mass spectral fragmentation patterns of the group 14 organometallic compounds.

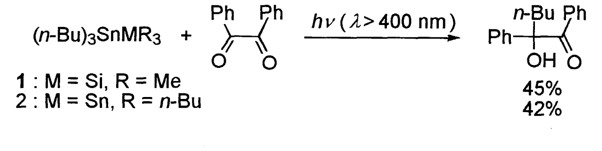


Irradiation of an acetonitrile solution of 1,2,4,5-tetracyanobenzene (TCNB) in the presence of tributyl(trimethylsilyl)stannane (**1**) with a medium-pressure mercury lamp through a filter gave 5-butyl-1,2,4-tricyanobenzene in 32% yield. Similarly, on irradiation of a propionitrile solution of TCNB and hexabutyldistannane (**2**), the same alkylated product was formed in 51% yield. However, in both the reactions, any stannylated or silylated products were not detected in the reaction mixtures.[7]

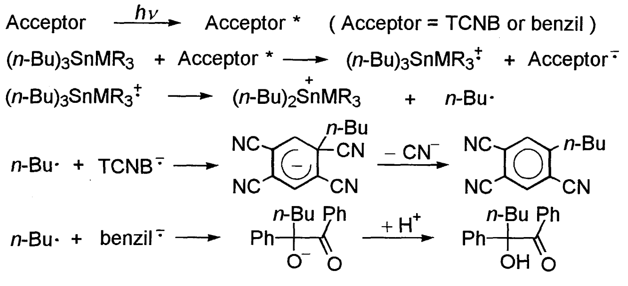


The fluorescence of TCNB was quenched by **1** (k_q = 2.0 x 10^{10} dm^3 mol^{-1} s^{-1}) and **2** (k_q = 1.7 x 10^{10} dm^3 mol^{-1} s^{-1}) nearly at the diffusion controlled rate in acetonitrile and propionitrile, respectively. Furthermore, highly exothermic free energy change for the electron transfer process from **1** and **2** to the excited singlet state of TCNB was calculated by the Rehm–Weller equation.[8] The results indicate that an electron is transferred from **1** and **2** to the excited singlet state of TCNB in the initial stage of the photoalkylation reactions.

The photoalkylation of benzil with **1** and **2** also proceeded. Thus, irradiation of an acetonitrile solution of **1** and benzil and a propionitrile solution of **2** and benzil gave the corresponding α-ketol in 45 and 42% yields, respectively. In both the reactions, any stannylated or silylated products were not also detected in the reaction mixtures.[7] Operation of electron transfer from **1** and **2** to the excited triplet state of benzil is shown by effective quenching of the photoalkylation reactions by anthracene and by the negative free energy change for the electron transfer process from **1** and **2** to the excited triplet state of benzil calculated by the Rehm–Weller equation.[8]

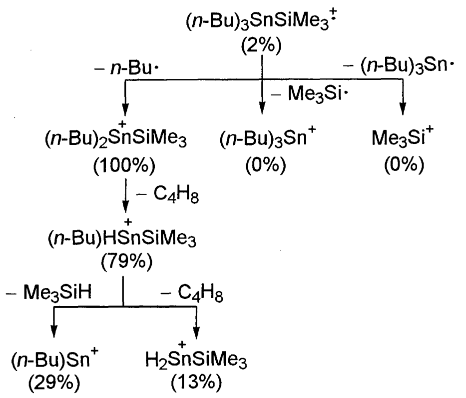


The photoalkylation is explained by the mechanism in Scheme 1. Electron transfer from **1** and **2** to the excited singlet state of TCNB or the excited triplet state of benzil affords the radical cation of **1** and **2** and the radical anion of TCNB or benzil. The radical cation is cleaved to the alkyl radical and the silyl-substituted stannyl cation or the distannanyl cation. The alkyl radical attacks the radical anion of TCNB or benzil, and substitution of the cyano group of TCNB or addition to the carbonyl group of benzil occurs as previously reported.[9]

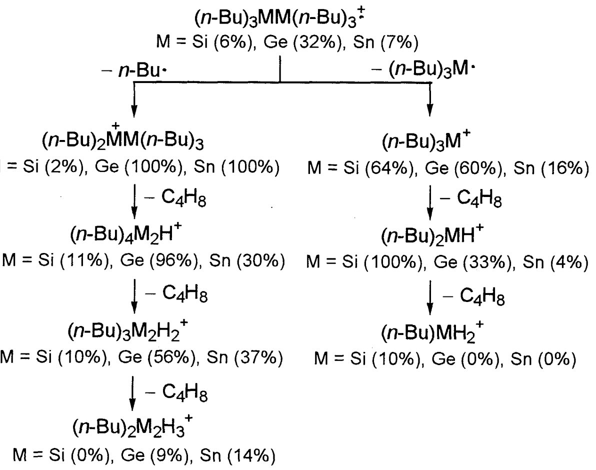


Scheme 1.

These results are in contrast with the photosilylation of aromatic nitriles with hexamethyldisilane.[1d] In this case, the Si–Si bond of the radical cation of hexamethyldisilane is cleaved and the trimethylsilyl group is preferentially introduced to aromatic nitriles. In order to gain information about cleavage of organodigermane, we attempted the similar photolysis of TCNB with hexabutyldigermane. However, only complex mixtures were obtained, and neither photoalkylated nor photogermylated product was obtained.



Scheme 2.



Scheme 3.

Since the analogy between photo-induced electron transfer and mass spectral fragmentation has been recognized,[9b,10] it would be interesting to compare the unexpected cleavage of the radical cation of the group 14 organometallics formed by photo-induced electron transfer with mass spectral fragmentation pattern.[11] In the mass spectrum of hexamethyldisilane, the molecular ion is cleaved to give the trimethylsilyl cation and the pentamethyldisilanyl cation in 100 and 26% intensities, respectively. Apparently, cleavage of the Si–Si bond is preferred to that of the Si–C bond. On the other hand, in the mass spectrum of **1**, the most prominent peak comes from the Sn–C bond fission of $\mathbf{1}^{+\cdot}$. The mass peaks corresponding to the Sn–Si bond cleavage cannot be observed (Scheme 2). Similar trends are observed in the series of mass spectral fragmentation of $(n\text{-Bu})_3\text{MM}(n\text{-Bu})_3$ (M = Si, Ge, Sn) (Scheme 3). In hexabutyldistannane, the main fragmentation process is cleavage of the Sn–C bond followed by successive elimination of the butyl groups. The tributylstannyl cation derived from the Sn–Sn bond fission is observed as a minor peak. On the contrary, in hexabutyldisilane, the major fragmentation process turns to cleavage of the Si–Si bond and the Si–C bond fission constitutes only the minor pathway. In the case of hexabutyldigermane, both the Ge–Ge and Ge–C bond fission proceeds rather comparably. These results show that in $R_3M\text{-}M'R'_3$ (M, M' = Si, Ge, and Sn), competition between cleavage of the matal–metal bond and the metal–carbon bond is highly dependent on the nature of the group 14 elements, and cleavage of the metal–carbon bond becomes more favorable in the order of Si, Ge, and Sn. The trends are in good accord with those in the chemistry of the radical cation of the group 14 organometallic compounds formed by photo-induced electron transfer.

This work was partially supported by a Grant-in-Aid on Priority-Area-Research "Photoreaction Dynamics" No. 623922 and a Grant-in-Aid for Encouragement of Young Scientists No. 02854054 from the Ministry of Education, Science and Culture.

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7 During the reactions, monostannanes might be formed by cleavage of the Sn–Si or Sn–Sn bond of **1** and **2**. However, none of these compounds were detected. This excludes possibility that the butyl group is introduced from the monostannanes.[9]

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11 Mass spectra were recorded on a Hitachi M-80B mass spectrometer by the electron ionization (EI) method at 10 eV of the ionizing energy. Each fragmentation pathway was confirmed by the linked-scan measurement (B/E and B^2/E).