Cleavage Mode of Benzyltributylstannane Radical Cations Produced in Photoinduced Electron Transfer

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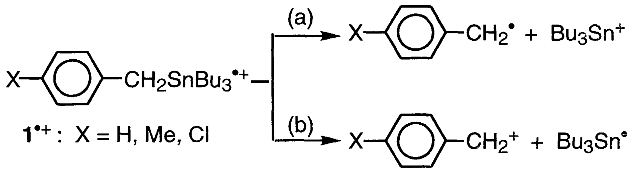
Cleavage of metal-carbon bond of benzyltributylstannane radical cation produced in photoinduced electron transfer from benzyltributylstannane to 10-methylacridinium ion occurs to give benzyl radical rather than benzyl cation, resulting in formation of 9-benzyl-10-methyl-9,10-dihydroacridine selectively in dehydrated acetonitrile. In the presence of water, however, 10-methyl-9,10-dihydroacridine is also formed via electron transfer from benzyl radical to the dihydroacridine radical cation produced by protonation of acridinyl radical following the initial photoinduced electron transfer.

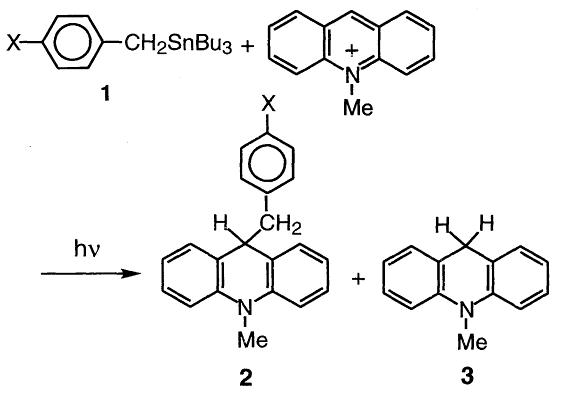
Electron transfer oxidation of group 14 organometallics (R_4M: M = Si, Ge, Pb; R = alkyl) is known to result in facile cleavage of the metal-carbon bond.[1] There are two possible modes of the metal-carbon bond cleavage in such reactions to generate (a) $R^\bullet$ and R_3M^+ or (b) R^+ and $R_3M^\bullet$. Eaton has proposed that two types of products are obtained by competition between two modes [(a) and (b)] of cleavage of the stannane radical cation produced in the reduction of tetracyanoethylene (TCNE) by benzyltributylstannanes as shown in Scheme 1.[2] However, the reduction of TCNE by R_4M has been shown to proceed via inner-sphere electron transfer rather than outer-sphere electron transfer.[3] In the photochemical reactions of benzyltributylstannanes with electron acceptors such as dicyanobenzenes and α-diketones, the benzyl adducts are obtained, when the cleavage of the stannane radical cation is proposed to give benzyl radical exclusively.[4] Thus, it is desired to examine the cleavage mode of benzyltrialkylstannane radical cation in the outer-sphere electron transfer reactions in order to clarify the intrinsic cleavage mode of the stannane radical cations.

This study reports that two types of products are obtained in the photoreduction of 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$) by benzyltributylstannanes **1** via outer-sphere electron transfer from **1** to the singlet excited state of $AcrH^+$ but that the cleavage of the metal-carbon bond of $\mathbf{1}^{\bullet+}$ results in formation of benzyl radical and stannane cation exclusively [path (a) in Scheme 1].

Visible light irradiation of the absorption band of $AcrH^+$ (1.0×10^{-2} mol dm^{-3}) in acetonitrile containing **1** (1.0×10^{-2} mol dm^{-3}) and water (3.6×10^{-2} mol dm^{-3}) for 24 h gave two types of products, 9-benzyl-10-methyl-9,10-dihydroacridine **2** and 10-methyl-9,10-dihydroacridine **3** (Eq. 1). The products are well identified by the ^{1}H NMR spectra.[5] Relative yields of **2** and **3** are shown in Table 1. At the first glance two types of products may be explainable in terms of competition between two modes of cleavage of the stannane radical cation produced by photoinduced electron transfer from **1** to $AcrH^+$ as shown in Scheme 2. The fragmentation of $\mathbf{1}^{\bullet+}$ into benzyl radical and the radical coupling with $AcrH^\bullet$ yields **2**, while that into $Bu_3Sn^\bullet$ yields the adduct which may be converted to **3** by the reaction with water. In such a case, both products should be formed through the common intermediate in a parallel manner. When the time course of the photoreaction is followed by HPLC, however, **2** is formed exclusively at the initial stage and **3** is formed only at prolonged irradiation time, when the relative yields of **2** decreases but the sum of the yields of **2** and **3** reaches 100%. In

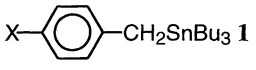


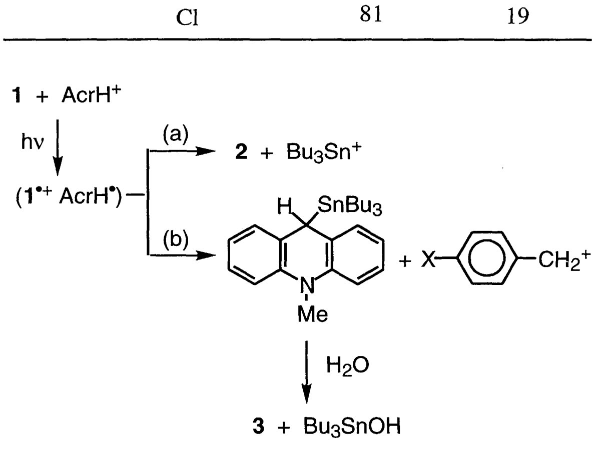
Scheme 1.



(1)

Table 1. Relative yields of products from the photoreduction of $AcrH^+$ by **1**

 **1**	Relative yield, %	
	2	**3**
X = H	46	54
Me	45	55
Cl	81	19

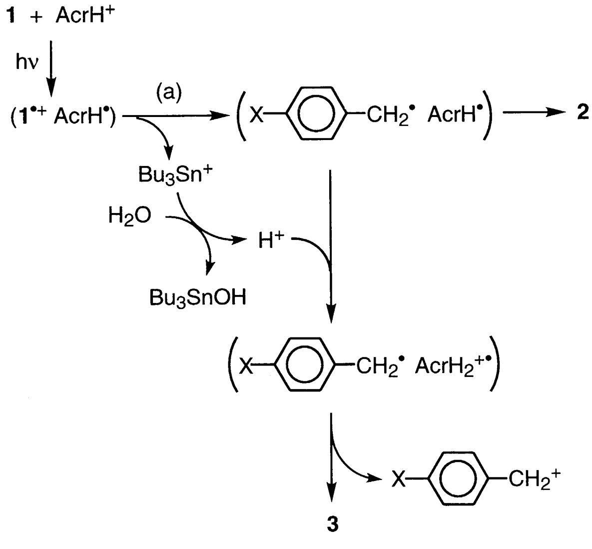


Scheme 2.

extensively dehydrated MeCN, no stannyl adduct was detected by ^1H NMR, but **2** was formed exclusively. Thus, **3** may be formed through the secondary reaction from the initial product.

We have recently shown that **3** is formed in the photochemical reaction of $AcrH^+$ with alkylbenzenes in the presence of $HClO_4$ in MeCN.[5] In the absence of $HClO_4$, the photoaddition of alkylbenzenes with $AcrH^+$ occurs to yield the corresponding benzyl adducts. Both reactions are initiated by photoinduced electron transfer from the alkylbenzene to the singlet excited state ($^1AcrH^{+*}$) to give the alkylbenzene radical cation and acridinyl radical ($AcrH^\bullet$). The deprotonation from the alkylbenzene radical cation gives the corresponding benzyl radical ($R^\bullet$). In the absence of $HClO_4$, the two radical species ($AcrH^\bullet$ and $R^\bullet$) couples efficiently to yield the adduct. On the other hand, $AcrH^\bullet$ is protonated in the presence of $HClO_4$ to give $AcrH_2^{\bullet +}$ which can accept an electron from $R^\bullet$ to yield **3** and R^+. The benzyl cation and analogs (R^+) undergo the nucleophilic addition of H_2O to yield the oxygenated product, i.e., the corresponding benzyl alcohol derivatives (ROH). In the present case as well, benzyl alcohol was formed accompanied by the formation of **3**.

Thus, formation of **3** at the prolonged irradiation time in the presence of water may be explained by the generation of H^+ from the initial product, Bu_3Sn^+ with H_2O as shown in Scheme 3. The outer-sphere electron transfer from **1** to $^1AcrH^{+*}$ may occur efficiently judging from the highly negative values of free energy change of electron transfer (ΔG^0_{et}). The ΔG^0_{et} values obtained from the one-electron oxidation potentials of **1**[6] and the reduction potential of $^1AcrH^{+*}$,[7] are listed in Table 2. In fact, the fluorescence of $^1AcrH^{+*}$ is quenched with the quenching rate constants (k_q) close to the diffusion-limited value (Table 1). From the saturated dependence of the quantum yields on [**1**] are also determined the rate constants (k_{obs}) and the limiting quantum yields (Φ_∞) as listed in Table 2. The k_{obs} values agree with the k_q values. Essentially the same results are obtained in the case of benzyltrimethylstannane as those of benzyltributylstannane.



Scheme 3.

Table 2. Free energy change ΔG^0_{et}, quenching rate constants k_q, observed rate constants k_{obs}, and limiting quantum yields Φ_∞ in the photoreduction of of $AcrH^+$ by **1**

1	ΔG^0_{et}, kJ mol^{-1}	k_q, $dm^3\ mol^{-1}\ s^{-1}$	k_{obs}, $dm^3\ mol^{-1}\ s^{-1}$	Φ_∞
X = H	-78	1.7×10^{10}	1.6×10^{10}	0.37
Me	-80	1.8×10^{10}	1.8×10^{10}	0.37
Cl	-52	1.5×10^{10}	1.4×10^{10}	0.41

Thus, the photochemical reaction proceeds via the outer-sphere electron transfer from **1** to $^1AcrH^{+*}$ to generate the radical pair ($\mathbf{1}^{\bullet +}$ $AcrH^\bullet$) in which the cleavage of the Sn-C bond occurs to give benzyl radical exclusively [path (a) in Scheme 1]. The radical coupling in the pair yields **2** selectively at the initial stage (Scheme 3). In the presence of H_2O, the reaction of the other product, Bu_3Sn^+ with H_2O produces H^+ by which $AcrH^\bullet$ is protonated to give $AcrH_2^{\bullet +}$. Since the oxidation potentials of benzyl radicals[8] are more negative than the reduction potential of $AcrH_2^{\bullet +}$,[9] facile electron transfer from benzyl radical to $AcrH_2^{\bullet +}$ may occur to yield **3** at the prolonged irradiation time.

In conclusion, the cleavage of the metal-carbon bond of $\mathbf{1}^{\bullet +}$ gives exclusively benzyl radical although two types of products (**2** and **3**) are obtained as shown in Scheme 3.

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References and Notes

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