

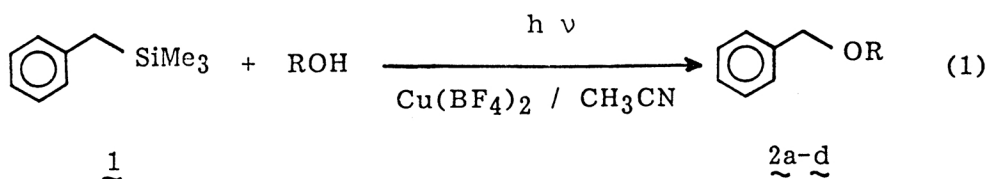
Generation of Organic Cations from Group 14 Organometallic Compounds
via Photoinduced Electron Transfer in the Presence of Cu(II) Salt

Kazuhiko MIZUNO,^{*} Masahiro YASUEDA, and Yoshio OTSUJI^{*}
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591

Irradiations of acetonitrile-alcohol (3 : 1) solutions of arylmethyl silanes, germane, or stannanes in the presence of $\text{Cu}(\text{BF}_4)_2$ gave alkyl arylmethyl ethers in good yields via arylmethyl cations. The efficiency of this photoreaction increased in the order of Si- < Ge- < Sn-compounds.

Recently, it has been demonstrated that a photoinduced one-electron transfer from allylic and benzylic silanes to organic electron acceptors produces allylic and benzylic radicals via their radical cations and the reactive species generated from this route have a wide applicability in organic synthesis.¹⁻³⁾ We now report that the photoreaction of group 14 organometallic compounds in the presence of Cu(II) salt generates organic cations via two-electron transfer.⁴⁻⁵⁾

Irradiation of a solution of benzyltrimethylsilane (1, 0.5 mmol) and 2 equiv. of copper(II) tetrafluoroborate ($\text{Cu}(\text{BF}_4)_2$, 1.0 mmol) in acetonitrile-methanol (3 : 1) with a 300 W high-pressure mercury lamp through a quartz filter for 10 h gave benzyl methyl ether (2a) in 70% yield, accompanying formation of $\text{CuBF}_4(\text{CH}_3\text{CN})_4$.⁶⁾ Similar irradiations of 1 in the presence of various kinds of



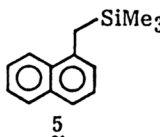
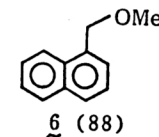
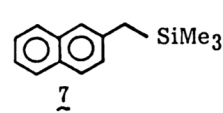
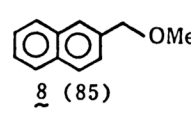
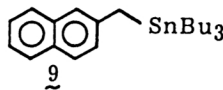
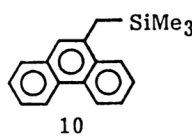
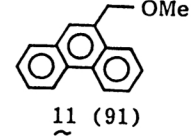
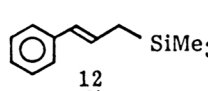
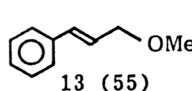
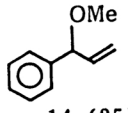
a; R = Me, b; R = Et, c; R = i-Pr, d; R = t-Bu

alcohols afforded the corresponding alkyl benzyl ethers (2b-d) (Table 1).

The controlled experiments showed that (1) in the absence of $\text{Cu}(\text{BF}_4)_2$, no reaction occurred with a quantitative recovery of 1, (2) the yield of 2a decreased but the yield of 1,2-diphenylethane increased, with decreasing the added amount of $\text{Cu}(\text{BF}_4)_2$ (Table 2), (3) no reaction occurred in the dark, and (4) no reaction also occurred for 1 when the photoreaction was carried out by employing Pyrex (>280 nm)

and uranyl (> 320 nm) filters, although UV spectrum of a mixture of 1 and $\text{Cu}(\text{BF}_4)_2$ in $\text{CH}_3\text{CN}-\text{MeOH}$ (3 : 1) showed a weak CT band in 290 - 350 nm region. It was, however, found that the photoreaction occurs with > 280 nm light for compounds 5, 7, 9, and 10 which absorb light in this region. The products were isolated by distillation under reduced pressure or column chromatography on silica gel. The structures of the products were assigned from their analytical and spectral (^1H NMR, mass) properties.

Table 1. Photoreaction of Group 14 Organometallic Compounds in the Presence of $\text{Cu}(\text{BF}_4)_2$

Compd	$E_{p/2}^{\text{ox}}$ /V ^{a)}	Alcohol	Irradiation		Product(s) (Yield/%) ^{b)}
			λ /nm	Time/h	
<u>1</u>	1.22	MeOH	> 200	10	<u>2a</u> (70)
<u>1</u>		EtOH	> 200	10	<u>2b</u> (48)
<u>1</u>		i-PrOH	> 200	10	<u>2c</u> (46)
<u>1</u>		t-BuOH	> 200	10	<u>2d</u> (98)
<u>3</u>	1.15	MeOH	> 200	4	<u>2a</u> (67)
<u>4</u>		MeOH	> 200	1.5	<u>2a</u> (94)
 <u>5</u>	0.96	MeOH	> 280	43	 <u>6</u> (88)
 <u>7</u>	0.96	MeOH	> 280	30	 <u>8</u> (85)
 <u>9</u>	0.60	MeOH	> 280	3	<u>8</u> (78)
 <u>10</u>	0.94	MeOH	> 280	40	 <u>11</u> (91)
 <u>12</u>	0.91	MeOH	> 200	15	 <u>13</u> (55) +  <u>14</u> (25)

a) Oxidation Potentials vs. Ag/Ag^+ in CH_3CN .

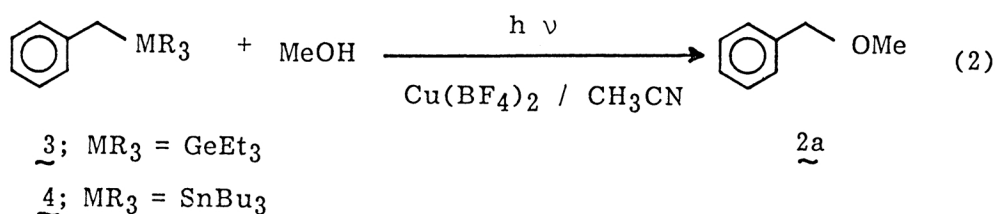
b) Yields based on Si-, Ge-, Sn-compounds used.

Table 2. Effect of the Concentration of $\text{Cu}(\text{BF}_4)_2$ on the Photoreaction of $\underline{1}$ in $\text{MeOH}-\text{CH}_3\text{CN}$ ^{a)}

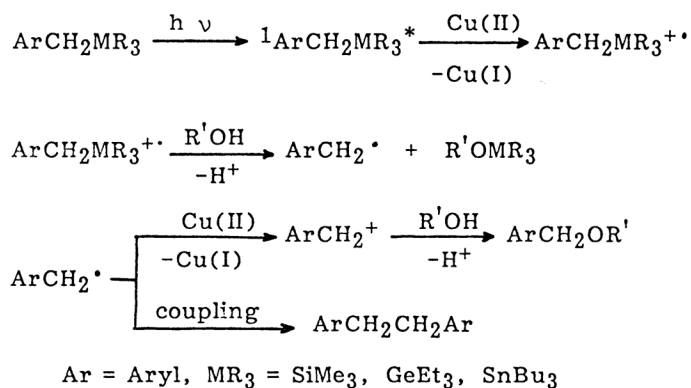
Molar ratio		Total yield of products/%	Product ratio	
$\underline{1}$	$\text{Cu}(\text{BF}_4)_2$		$\underline{2a}$	1,2-Diphenylethane
1	: 0.25	17	13	: 87
1	: 0.5	24	25	: 75
1	: 1	65	74	: 26
1	: 2	70	100	: 0

a) The reaction conditions were the same as those described in the text except the added amount of $\text{Cu}(\text{BF}_4)_2$. Irradiation time: 10 h.

Benzyltriethylgermane ($\underline{3}$) and benzyltributylstannane ($\underline{4}$) ⁷⁾ were also reactive for this photoreaction and they were converted into $\underline{2a}$ in good yields (Eq. 2). ⁸⁾ The efficiency of the photoreaction increased with decreasing oxidation potentials of organometallic compounds: i.e., the reactivity increased in the order of $\text{Si-} < \text{Ge-} < \text{Sn-}$ compounds (Table 1).



When 1- and 2-naphthylmethyl and 9-phenanthrylmethyl trimethylsilanes were irradiated through Pyrex in $\text{CH}_3\text{CN}-\text{MeOH}$ (3 : 1), the corresponding arylmethyl methyl ethers were obtained in high yields. Similar irradiation of (E)-3-phenyl-2-propenyltrimethylsilane ($\underline{12}$) gave $\underline{13}$ and $\underline{14}$ in a 2 : 1 ratio (Table 1).



Scheme 1.

The above photoreactions can be explained in terms of the mechanism involving electron transfer as shown in Scheme 1. The photoreaction is initiated by an exothermic one-electron transfer from the excited singlet organometallic compound ($^1\text{ArCH}_2\text{MR}_3^*$) to Cu(II) ion to give the radical cation $\text{ArCH}_2\text{MR}_3^{+\cdot}$ and Cu(I) ion. The radical cation dissociates to the arylmethyl radical ArCH_2^\cdot and the organometallic cation R_3M^+ . When the concentration of Cu(II) is high, ArCH_2^\cdot is oxidized further by the Cu(II) to the cation ArCH_2^+ which is converted to the ether compound by the reaction with alcohol.⁹⁾ At low concentration of Cu(II), 1,2-diarylethanes are predominantly formed by coupling of the radicals.

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References

- 1) K. Ohga and P. S. Mariano, *J. Am. Chem. Soc.*, **104**, 617(1982); K. Ohga, U. C. Yoon, and P. S. Mariano, *J. Org. Chem.*, **49**, 213(1984).
- 2) K. Mizuno, M. Ikeda, and Y. Otsuji, *Tetrahedron Lett.*, **1985**, 461; K. Mizuno, K. Terasaka, M. Ikeda, and Y. Otsuji, *ibid.*, **1985**, 5819.
- 3) Y. Kubo, T. Imaoka, T. Shiragami, and T. Araki, *Chem. Lett.*, **1986**, 1749.
- 4) S. Murai and S. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **39**, 198(1966); M. Kojima, H. Sakuragi, and K. Tokumaru, *ibid.*, **58**, 521(1985); K. Mizuno, J. Ogawa, H. Kagano, and Y. Otsuji, *Chem. Lett.*, **1981**, 437; K. Mizuno, K. Yoshioka, and Y. Otsuji, *ibid.*, **1983**, 941; K. Mizuno, K. Yoshioka, and Y. Otsuji, *J. Chem. Soc., Chem. Commun.*, **1984**, 1965.
- 5) The electrochemical oxidation of allylic and benzylic silanes has recently been reported: J. Yoshida, T. Murata, and S. Isoe, *Tetrahedron Lett.*, **1986**, 3373; T. Koizumi, T. Fuchigami, and T. Nonaka, *Chem. Express*, **1**, 355(1986); H. J. Schaefer, D. Hermeling, and K. H. Lange, *Spring Meeting of the Electrochemical Society, Cincinnati, Ohio Extended Abstracts(1984)*, p. 441.
- 6) $\text{CuBF}_4(\text{CH}_3\text{CN})_4$ complex was isolated as white precipitate in 80 - 90% yield: B. J. Hathaway, D. G. Hohal, and J. D. Postlethwaite, *J. Chem. Soc.*, **1961**, 3215.
- 7) R. M. Borg and P. S. Mariano, *Tetrahedron Lett.*, **27**, 2821(1986); K. Maruyama, H. Imahori, A. Osuka, A. Takuwa, and T. Tagawa, *Chem. Lett.*, **1986**, 1719; K. Mizuno, S. Toda, and Y. Otsuji, *ibid.*, **1987**, 203; K. Mizuno, S. Toda, and Y. Otsuji, *Nippon Kagaku Kaishi*, **1987**, 1183.
- 8) No reaction occurred with the Si- and Ge-compounds **1** and **3** in the dark. However, the Sn-compounds reacted even in the dark, though the rate of the dark reaction was much slower than that of the photoreaction.
- 9) Irradiation of an acetonitrile solution of **1** and $\text{Cu}(\text{BF}_4)_2$ in the absence of an alcohol gave N-benzylacetoamide in 59% yield, accompanying a small amount of benzyl alcohol. This result also supports the generation of organic cation from **1**.

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