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# Anodic Oxidation of α-Alkoxycarbonyloxy and α-Acyloxy Organotin Compounds

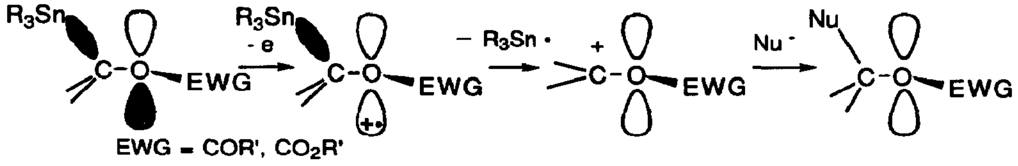
**Jun-ichi Yoshida,* Yuko Morita, Yuji Ishichi, and Sachihiko Isoe***

Department of Material Science, Faculty of Science, Osaka City University
Sugimoto 3-3-138, Sumiyoshi, Osaka 558, Japan

**Abstract:** *Electrochemical behavior of α-alkoxycarbonyloxy and α-acyloxy organotin compounds was studied. Preparative anodic oxidation in the presence of allylsilanes or silyl enol ethers gave the corresponding coupling products.*

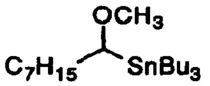
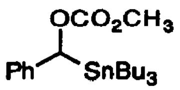
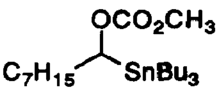
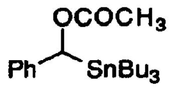
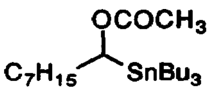
Recently we have revealed that the introduction of a stannyl group onto the carbon adjacent to the oxygen atom of ethers results in significant decrease in their oxidation potentials and that anodic oxidation of α-alkoxy organotin compounds results in the cleavage of the carbon-tin bond and the introduction of nucleophiles onto the carbon.[1,2] In this paper we wish to report on anodic oxidation of α-alkoxycarbonyloxy and α-acyloxy organotin compounds. Our purpose in this study is twofold. First, we wish to reveal whether the ability of tin to promote the electron transfer from β-situated oxygen atom is applicable to carbonates and esters which have an electron-withdrawing group on the oxygen. The introduction of an electron-withdrawing group on the oxygen atom lowers the energy level of its nonbonding p orbital to increase the energy difference between the oxygen p orbital and the C-Sn σ orbital.[3] So, their interaction is expected to become weaker to disfavor the electron transfer. The second purpose of the present study is to investigate the reactivity of carbocations generated by anodic oxidation of tin-substituted carbonates and esters. If the reaction proceeds in a similar manner to that of α-alkoxy organotin compounds, the carbon-tin bond of the initially formed cation radical is cleaved to generate the corresponding carbocation intermediates substituted by an alkoxycarbonyloxy or an acyloxy group (Scheme I). The introduction of an electron-withdrawing group on the oxygen atom is expected to destabilize the carbocation intermediates. The reactivity of such carbocations receives interests from view points of both mechanistic studies and synthetic utility.

**Scheme I.**



α-Alkoxycarbonyloxy and α-acyloxy organotin compounds were readily synthesized from the corresponding α-hydroxy organotin compounds prepared by the reaction of the corresponding aldehydes with a stannyl anion. Oxidation potentials of α-alkoxycarbonyloxy and α-acyloxy organotin compounds and related compounds were determined by rotating-disk electrode voltammetry. As shown in Table 1, oxidation potentials of aliphatic α-alkoxycarbonyloxy and α-acyloxy organotin compounds are more positive than the corresponding α-alkoxy organotin compounds, but less positive than those of tetraalkyltin. Oxidation potentials of simple aliphatic carbonates and esters are also very high (> 2.5 V). Therefore, tin and oxygen act cooperatively to reduce the oxidation potential. Oxidation potentials of benzylic α-alkoxycarbonyloxy and α-acyloxy organotin compounds, however, are more positive than benzyltributyltin.

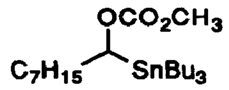
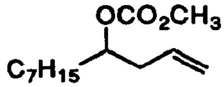
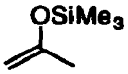
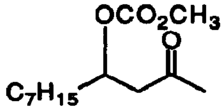
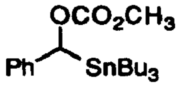
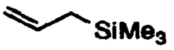
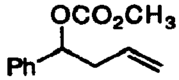
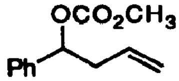
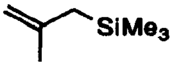
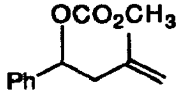
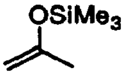
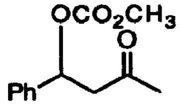
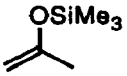
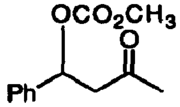
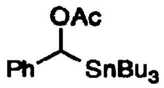
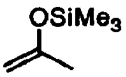
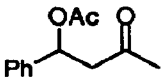
**Table 1.** Oxidation Potentials of α-Alkoxycarbonyloxy and α-Acyloxy Organotin Compounds [a]

| compound | $E_d$ (V) [b] | $E_{1/2}$ (V) [c] | compound | $E_d$ (V) [b] | $E_{1/2}$ (V) [c] |
|---|---|---|---|---|---|
|  | 0.84 | 0.97 |  | 0.84 | 1.00 |
|  | 1.33 | 1.47 |  | 0.87 | 0.98 |
|  | 1.29 | 1.44 |  | 0.61 | – |
| $Bu_4Sn$ | 1.36 | 1.52 | | | |

[a] The oxidation potentials were determined by rotating-disk electrode voltammetry in $LiClO_4$ / $CH_3CN$ using a glassy carbon working electrode and a Ag/AgCl reference electrode. [b] Decomposition potentials. [c] Half-wave potentials.

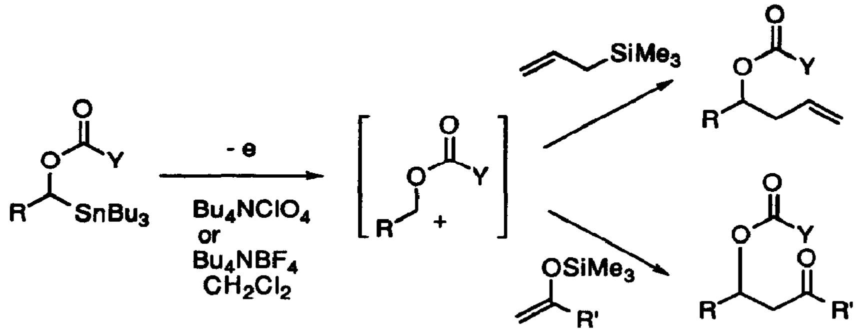
We have recently revealed that anodic oxidation of α-alkoxy organotin compounds in the presence of allylsilanes or silyl enol ethers gives the corresponding coupling products.[1c] Therefore, similar reactions of α-alkoxycarbonyloxy and α-acyloxy organotin compounds were examined. Constant current electrolysis in the presence of allylsilanes and silyl enol ethers proceeded smoothly giving rise to the facile cleavage of the carbon-tin bond and the introduction of carbon nucleophiles onto the carbon as shown in Scheme II and Table 2. The success of the present reaction indicates that carbocation intermediates substituted by $-OCO_2R$ or -OCOR group react effectively with allylsilanes and silyl enol ethers even though they have an electron-withdrawing group on the oxygen atom. As the supporting electrolyte, both tetrabutylammonium perchlorate and tetrabutylammonium tetrafluoroborate were effective, although the former seemed to give better yields of the coupling products.

**Table 2.** Anodic Oxidation of α-Alkoxycarbonyloxy and α-Acyloxy Organotin Compounds in the Presence of Allylsilanes or Silyl Enol Ethers [a]

| substrate | nucleophile | supporting electrolyte | electricity (F/mol) | product | yield (%) [b] |
|---|---|---|---|---|---|
|  |  | $Bu_4NClO_4$ | 2.5 |  | 68 [c] |
| |  | $Bu_4NClO_4$ | 3.2 |  | 52 |
|  |  | $Bu_4NBF_4$ | 3.0 |  | 86 |
| |  | $Bu_4NClO_4$ | 2.5 |  | 89 |
| |  | $Bu_4NClO_4$ | 2.2 |  | 73 |
| |  | $Bu_4NBF_4$ | 3.0 |  | 54 |
| |  | $Bu_4NClO_4$ | 2.2 |  | 94 |
|  |  | $Bu_4NClO_4$ | 2.4 |  | 70 |

[a] Reactions were normally carried out with an organotin compound (0.25 mmol) and an allylsilane or a silyl enol ether (1.25 mmol) in 2.5 ml of 0.2 M $Bu_4NClO_4$ or $Bu_4NBF_4$ / $CH_2Cl_2$ in an undivided cell equipped with a carbon rod anode and a platinum plate cathode under constant current conditions. [b] Isolated yields. [c] The electrochemical reaction was initiated in the presence of 1 equiv of allyltrimethysilane. After 1 F/mol of electricity was consumed, 1 equiv of allyltrimethylsilane was added, and after 2 F/mol of electricity was consumed, additional 1 equiv of allyltrimethylsilane was added.

**Scheme II.**



Recently organometallic compounds having a heteroatom substituent such as acyloxy group at the α-positon are utilized as important intermediates in organic synthesis.[4] For example, α-acyloxy organostannanes have been reported to undergo cross-coupling reactions with acyl chlorides in the presence of Pd / Cu catalysts.[4a] In such cases α-acyloxy organometallic compounds serve as α-acyloxy carbanion equivalents. The present electrochemical reaction provides an efficient method for umpolung[5] of such organometallics to afford α-carbonyloxy and α-alkoxycarbonyloxy carbocation equivalents, and promises to complement to the metal-promoted cross-coupling reactions.

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## References and Notes

1. (a) Yoshida, J.; Ishichi, Y.; Nishiwaki, K.; Shiozawa, S.; Isoe, S. *Tetrahedron Lett.* **1992**, *33*, 2599. (b) Yoshida, J.; Ishichi, Y.; Isoe, S. *J. Am. Chem. Soc.* **1992**, *114*, 7594. (c) Yoshida, J.; Itoh, M.; Isoe, S. *J. Chem. Commun.* **1993**, 547.
2. Chemical electron-transfer reactions of α-heteroatom-substituted organotin compounds have also been studied. For example, (a) Narasaka, K.; Okauchi, T.; Arai, N. *Chem. Lett.* **1992**, 1229. (b) Takeda, T.; Kanamori, F.; Masuda, M.; Fujiwara, T. *Tetrahedron Lett.* **1991**, *32*, 5567.
3. The interaction of a C-Si σ orbital with nonbonding p orbital of an oxygen atom has been studied extensively: Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962.
4. For example, (a) Ye, J.; Bhatt, R. K.; Falck, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 1. (b) Knochel, P.; Chou, T.-S.; Jubert, C.; Rajagopal, D. *J. Org. Chem.* **1993**, *58*, 588.
5. For example, Seebach, D.; Enders, D. *Angew. Chem.* **1975**, *87*, 1.

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