Tetrahedron Letters, Vol. 33, No. 18, pp. 2599-2602, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

Electrochemical Oxidation of α-Alkoxystannanes

Jun-ichi Yoshida,* Yuji Ishichi, Keiji Nishiwaki, Satoshi Shiozawa, and Sachihiko Isoe*

Institute of Organic Chemistry, Faculty of Science, Osaka City University, Sugimoto 3-3-138, Sumiyoshi, Osaka 558

Key Words: α-alkoxystannane, β-effects in electron transfer reactions, electrochemical oxidation, oxidation potential

Abstract: *The introduction of tin on the carbon adjacent to the oxygen of aliphatic ethers results in significant decrease in the oxidation potentials. The effect of tin is much larger than that observed for silicon. Preparative electrochemical oxidation of α-alkoxystannanes results in selective cleavage of the carbon-tin bond and introduction of a nucleophile such as an alcohol onto the carbon.*

Increasing attention has been paid for the silicon β-effects in electron-transfer reactions, the ability of silyl groups to promote the electron transfer from heteroatoms β to silicon.[1] The interaction of the carbon-silicon σ orbital with the non-bonding *p* orbital of the heteroatom raises the HOMO level which in turn favors the electron transfer (Fig. 1). In this paper we wish to report that tin also promotes the electron transfer from the oxygen at β position.

Several α-alkoxystannanes were synthesized and their oxidation potentials were determined by rotating disk electrode (RDE) voltammetry[2] in 0.1 M $LiClO_4/CH_3CN$ using a glassy carbon electrode (Table 1).

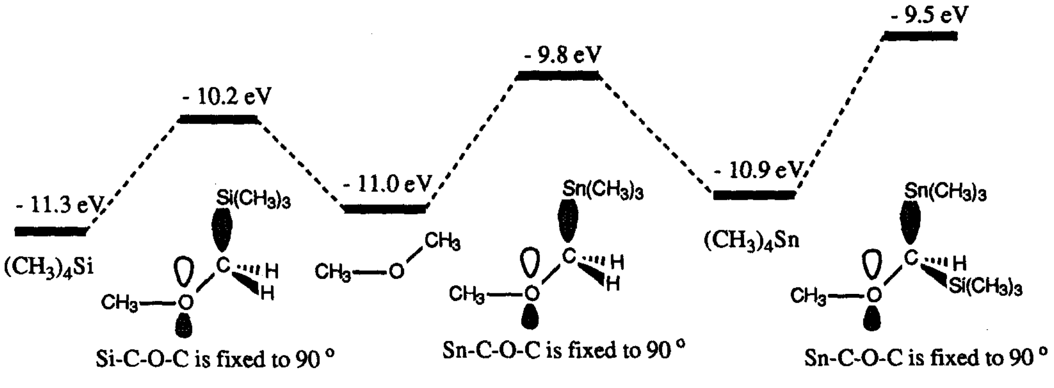
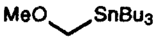
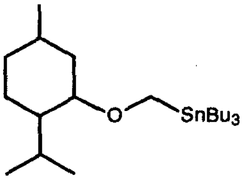
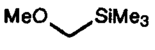
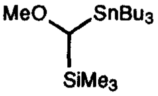
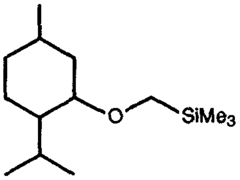
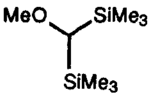


Figure 1. HOMO level diagram of α-alkoxystannanes and α-alkoxysilanes calculated by MNDO method.

Table 1. Oxidation Potentials of α-Alkoxystannane and Related Compounds[a]

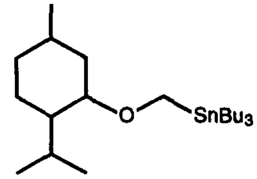
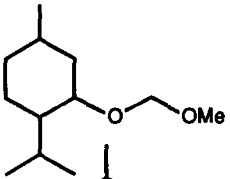
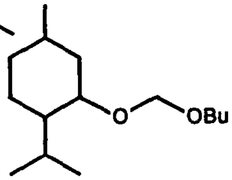
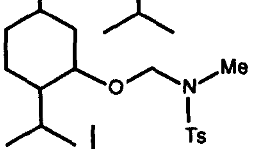
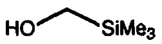
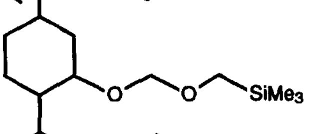
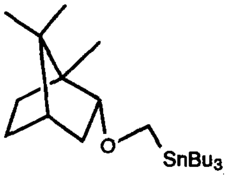
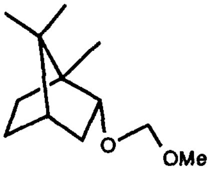
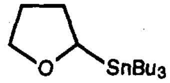
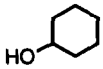
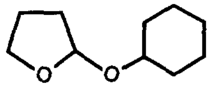
compound	$E_{1/2}$ (V vs Ag/AgCl)	compound	$E_{1/2}$ (V vs Ag/AgCl)
	1.14		1.09
	1.85		
	1.00		1.83
	1.54		1.29
Bu_4Sn	1.52		ca. 1.9

[a] Determined by rotating disk electrode method using a glassy carbon electrode in 0.1 M $LiClO_4$ / CH_3CN

Generally, it is difficult to oxidize aliphatic ethers electrochemically because their oxidation potentials are high (> 2.5 V vs Ag/AgCl).[3] Introduction of a stannyl group on the carbon adjacent to the oxygen atom, however, results in dramatic decrease in the oxidation potential. The oxidation potentials of α-alkoxystannanes are much less than the corresponding α-alkoxysilanes. For example, (methoxymethyl)tributylstannane exhibits an oxidation wave at the half wave potential of 1.14 V, whereas the half wave oxidation potential of (methoxymethyl)trimethylsilane is 1.85 V. The oxidation potential of tetrabutylstannane[4] (1.52 V) is higher than those of α-alkoxystannanes. Decrease of oxidation potentials seems to be attributed to the rise of the HOMO level by the interaction of the carbon-tin σ bond and the nonbonding *p* orbital of the oxygen atom (Fig. 1).[5] It is also worth noting that the oxidation potential of the compound having both tin and silicon on the same carbon is less than that having only tin, indicating cooperative effect of tin and silicon.

Preparative electrochemical oxidation reactions of α-alkoxystannanes were carried out in an undivided cell equipped with a carbon rod anode and a platinum plate cathode. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was used as supporting electrolyte and dichloromethane (CH_2Cl_2) was used as solvent. The reaction took place smoothly in the presence of an oxygen nucleophile such as methanol. The carbon-tin bond was cleaved selectively and the nucleophile was introduced onto the carbon, giving the corresponding mixed acetals in good to excellent yields (Table 2). Nitrogen nucleophiles such as tosylamides were also effective. It should be noted that compounds which are not suitable as nucleophiles in the electrochemical oxidation of

Table 2. Electrochemical Oxidation of α-Alkoxystannanes

compound	nucleophile (eq)	electricity (F/mol)	product	yield (%)[a]
	MeOH (4.3)	4.0		90
	BuOH (2.0)	3.3		95
	TsNHMe (2.9)	3.5		55
	 (3.0)	2.8		75
	MeOH (3.0)	3.8		73
	 (2.5)	2.3		90[b]

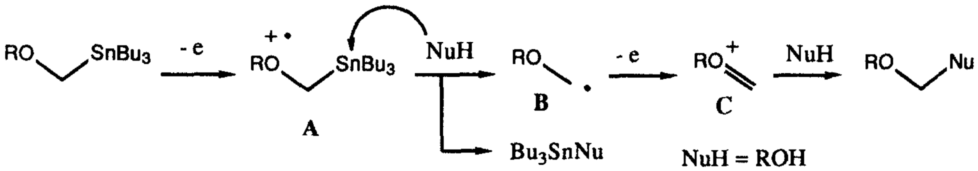
[a] Isolated yields. [b] The reaction was carried out in THF.

α-alkoxysilanes because of their low oxidation potentials can be used in the electrochemical oxidation of α-alkoxystannanes. For example, the oxidation potential of (hydroxymethyl)trimethylsilane is comparable to those of α-alkoxysilanes. Therefore, (hydroxymethyl)trimethylsilane is not suitable as a nucleophile in the electrochemical oxidation of α-alkoxysilanes. The oxidation potentials of α-alkoxystannanes are, however, much less than that of (hydroxymethyl)trimethylsilane. Thus the electrochemical oxidation of (menthyloxymethyl)tributylstannane took place smoothly in the presence of (hydroxymethyl)trimethylsilane to give the corresponding mixed acetal without affecting the carbon-silicon bond.

The mechanism which is analogous to that proposed for the electrochemical oxidation of α-alkoxysilanes[8] seems to be reasonable (Scheme I). The initial one-electron transfer produces the cation radical species A. The nucleophile attacks the tin atom to cleave the carbon-tin bond affording the carbon radical species

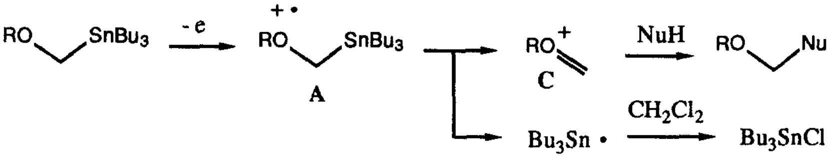
B which is immediately oxidized electrochemically to give the cation **C**. The cation **C** is then reacts with the nucleophile such as methanol to give the final product.

Scheme I.



Another possibility to be considered is that the carbon-tin bond in the cation radical **A** is cleaved homolytically to give the cation **C** directly together with the stannyl radical (Scheme II).

Scheme II.



Since Bu_3SnCl was obtained as a byproduct (45% isolated yield) in the reaction of (menthyloxymethyl)-tributylstannane with butanol, the second mechanism involving the homolytic cleavage of the C-Sn bond generating the stannyl radical seems to be more plausible. In this case probably the stannyl radical abstracted chlorine atom from dichloromethane, because polyhalomethanes are known to be effective radical scavengers.[9] Further studies on the origin of the marked effect of tin in electron-transfer reactions and the mechanism of the electrochemical oxidation of α-alkoxystannanes are in progress.

Acknowledgment. We thank the Ministry of Education, Science, and Culture, Japan for Grant-in-Aid for Scientific Research on Priority Area (No. 03233228) for partial financial support.

References and Notes

1. Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962 and references cited therein.
2. Rotating disk electrode voltammetry of organotin compounds: See Abeed, F. A.; Al-Allaf, T. A. K.; Ahmed, K. S. *Appl. Organomet. Chem.* **1990**, *4*, 133 and references cited therein.
3. Shono, T. in "The chemistry of ethers, crown ethers, hydroxyl groups and their sulphur analogues, Part 1", Patai S. Ed, Wiley, Chichester, 1980, Chapt 8.
4. Oxidation potentials of tetraalkylstannane determined by cyclic voltammetry was reported by Kochi et al.: Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790.
5. Although it has been reported that the ionization potentials of organostannanes obtained by MNDO calculations are systematically larger than the experimental values,[6] the energy of HOMO obtained by MNDO calcualtions[7] are consistent with the experimental oxidation potentials qualitatively.
6. Dewar, M. J. S.; Grady, G. L.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1984**, *106*, 6771.
7. MOPAC Ver. 5, Stewart, J. J. P., QCPE #455; Revised as Ver. 5.01 by Tsuneo Hirano, University of Tokyo, for HITAC and Unix machines, *JCPE Newsletter*, **1989**, *1*, 36; Revised as Ver. 5.02 by Jun-ichi Yoshida, Osaka City University, for NDP Fortran.
8. Yoshida, J.; Murata, T.; Isoe, S. *J. Organomet. Chem.* **1988**, *345*, C23.
9. Sakurai, H.; Mochida, K.; Hosomi, A.; Mita, F. *J. Organomet. Chem.* **1972**, *38*, 275.

(Received in Japan 6 February 1992)