Competition between Electroauxiliaries. Selective Electrochemical Oxidation of Heteroatom Compounds Having Silicon and Tin on the Same Carbon

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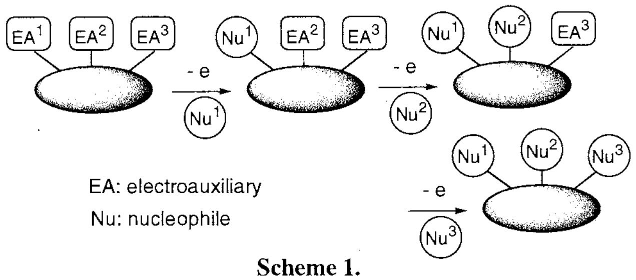
The selective electrochemical oxidation of heteroatom compounds having two different types of electroauxiliaries, *i.e.* silicon and tin on the same α carbon has been achieved. The C-Sn bond was cleaved selectively and a nucleophile was introduced. The second oxidation of the compound thus obtained gave rise to the cleavage of the C-Si bond and the introduction of a second nucleophile. The present study indicates the feasibility of the redox potential based strategies using electroauxiliaries.

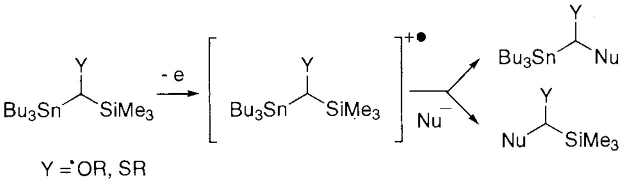
Recently we proposed the concept of electroauxiliary as a useful tool in electron transfer based organic synthesis.[1] An electroauxiliary is an auxiliary that activates substrate molecules toward electron transfer, controls the fate of thus generated reactive intermediates such as cation radicals and anion radicals, and then biases the formation of desired products. Group 14 elements such as silicon and tin serve as effective electroauxiliaries in the electrochemical,[2] chemical,[3] and photochemical[4] electron transfer reactions of heteroatom compounds.[5]

Although the cases where the substrate molecule has only one electroauxiliary have been studied extensively, little work has been done for the case where the substrate molecule has more than two electroauxiliaries. Selective utilization of one of the electroauxiliaries in the first reaction followed by the subsequent sequential utilization of other electroauxiliaries would lead to the selective transformation based on the redox potentials of electroauxiliaries (Scheme 1).



Scheme 1.

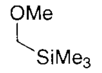
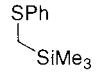
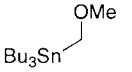
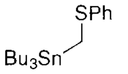
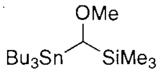
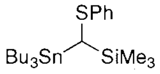
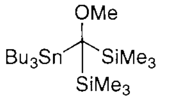
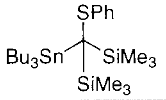
In our project aimed at redox potential based strategies, we studied the most simple case where a substrate molecule has two classes of electroauxiliaries, silicon and tin. In this paper we wish to report the study of the competition between silicon and tin on the same α-carbon in the electrochemical oxidation of heteroatom compounds (Scheme 2).



Scheme 2.

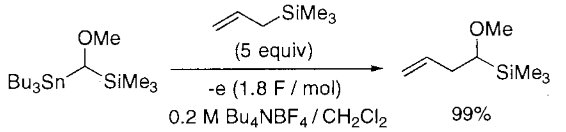
We first examined the oxidation potentials using rotating disk electrode voltammetry. As shown in Table 1 the oxidation potentials of the ethers and sulfides having both silicon and tin were less positive than those of the corresponding compounds having only silicon and similar to those for having only tin. This result indicates that the interaction between silicon and tin is very weak.

Table 1. Oxidation potentials of ethers and sulfides having the silyl group and the stannyl group as electroauxiliaries [a]

substrate	Ed / V	substrate	Ed / V
	1.60		1.12
	0.91		0.69
	0.90		0.62
	0.80		0.69

[a] The oxidation potentials (decomposition potentials) were determined with rotating disk electrode voltammetry using a glassy carbon working electrode and a SCE reference electrode in 0.1 M $LiClO_4/CH_3CN$.

Next we examined the selectivity of the bond cleavage. Preparative electrochemical oxidation reaction of methoxy(trimethylsilyl)(tributylstannyl)methane was carried out in the presence of allyltrimethylsilane as a carbon nucleophile.[6] The reaction took place smoothly giving rise to the selective cleavage of the C-Sn bond and the introduction of the allyl group on the carbon (eq 1). The C-Si bond was not affected at all.



(1)

The observed selective C-Sn bond cleavage is consistent with the results of molecular orbital calculations (MP2/LANL2DZ).[7] The geometry optimization of the cation radical of the model compound gave two structures (**A** and **B**) as shown in Figure 1. In both structures the C-Sn σ orbital interacts

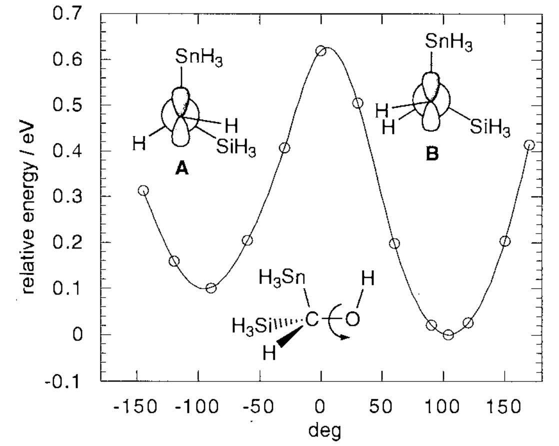
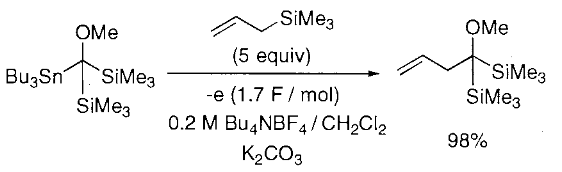


Figure 1. Plots of relative energy of the cation radical of $(H_3Sn)(H_3Si)CHOH$ vs. torsion angle of Sn-C-O-H.

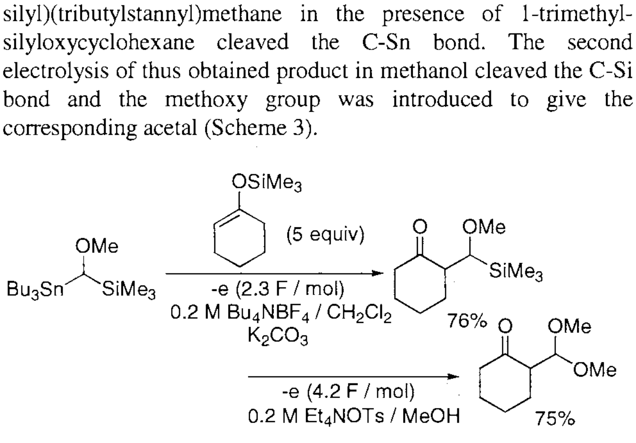
with the p orbital of the oxygen. The calculations also indicated that the C-Sn bond is significantly elongated whereas the C-Si bond length is rather close to the normal bond length,[8] suggesting that the selective cleavage of the C-Sn bond takes place.

The selective C-Sn bond cleavage was also accomplished for the compound having two silyl groups and one stannyl group. The anodic oxidation of methoxybis(trimethylsilyl)(tributylstannyl)-methane in the presence of allyltrimethylsilane gave the allylated compound in excellent yield (eq 2).



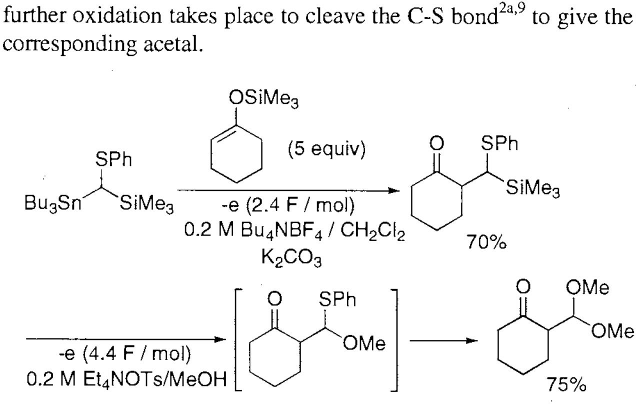
(2)

The sequential introduction of two nucleophiles was achieved by the sequential electrolysis with different nucleophiles. For example, the electrochemical oxidation of methoxy(trimethylsilyl)(tributylstannyl)methane in the presence of 1-trimethylsilyloxycyclohexane cleaved the C-Sn bond. The second electrolysis of thus obtained product in methanol cleaved the C-Si bond and the methoxy group was introduced to give the corresponding acetal (Scheme 3).



Scheme 3.

This type of introduction of two nucleophiles using two different electroauxiliaries can also be applied for organosulfur compounds. Thus, the anodic oxidation of phenylthio(trimethylsilyl)(tributylstannyl)methane in the presence of 1-trimethylsilyloxycyclohexene cleaved the C-Sn bond selectively (Scheme 4). The subsequent anodic oxidation cleaved the C-Si bond. The further oxidation takes place to cleave the C-S bond[2a,9] to give the corresponding acetal.



Scheme 4.

The present study demonstrates the feasibility of the strategies using multiple electroauxiliaries of different redox potentials. Selective sequential transformation can be accomplished based on the redox potentials of the electroauxiliaries. Further studies concerning the applications of this concept in organic synthesis are underway.

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6 The anodic oxidation reaction was usually carried out in a divided cell equipped with a carbon felt anode and a platinum plate cathode or an undivided cell equipped with a carbon rod anode and a platinum plate cathode in 0.2 M Bu_4NBF_4 / CH_2Cl_2 in the presence of molecular sieves 4A.

7 Gaussian 94, Revision B.2, was used for the calculations.

8 The C-Sn bond is elongated by 11% in the cation radical whereas the C-Si bond is elongated by 3% in **B**.

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