Electrooxidative Coupling of α-Heteroatom-substituted Organostannanes and Organosilanes

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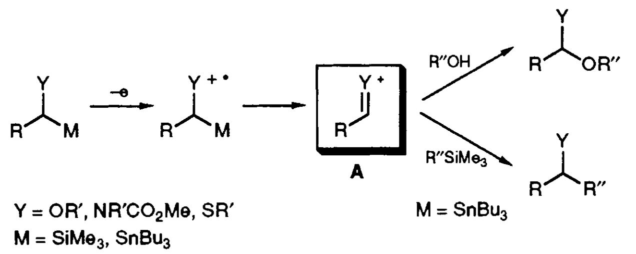
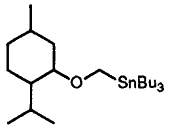
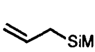
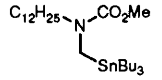
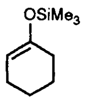
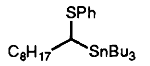
Anodic oxidation of α-heteroatom-substituted organostannanes in the presence of organosilanes such as allylsilanes and silyl enol ethers results in the facile cleavage of the carbon–tin bond and introduction of allyl and acyl groups onto the carbon, respectively.

Recently, electon-transfer reactions of α-heteroatom-substituted group 14 element compounds have received considerable attention.[1] Group 14 elements facilitate electron transfer from a β-heteroatom[2] and we have been interested in electrochemical electron-transfer reactions of α-heteroatom-substituted group 14 element compounds and have found that anodic oxidation of such compounds results in facile cleavage of the carbon–metal bond and introduction of a nucleophile such as an alcohol onto the carbon. A mechanism involving carbocation intermediate **A** has been suggested (Scheme 1).[3] However, the introduction of carbon nucleophiles by anodic oxidation of such compounds has remained an unexplored area of research, although effective carbon–carbon bond-forming reactions have been achieved by chemical[4] and



Scheme 1

Table 1 Oxidation potentials of α-heteroatom-substituted organostannanes and related compounds[a]

Compound	E_d/V	$E_{1/2}$/V	Compound	E_d/V	$E_{1/2}$/V
	0.94	1.09		1.53	1.70
	0.77	0.92		1.23	[b]
	0.63	0.74			

[a] Determined by rotating-disk voltammetry in $LiClO_4$–MeCN. Ag/AgCl was used as the reference electrode. [b] It was difficult to determine the half-wave potential.

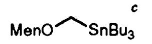
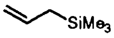
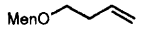
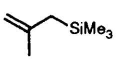
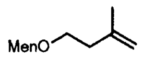
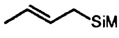
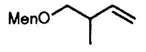
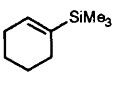
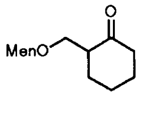
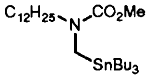
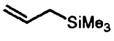
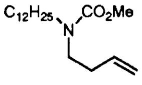
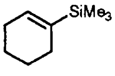
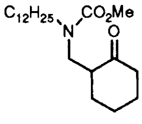
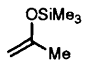
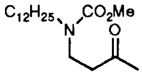
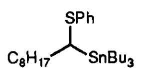
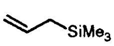
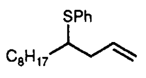
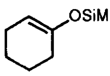
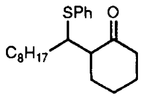
photochemical[5] electron-transfer reactions. Recently, we found that effective intramolecular carbon–carbon bond formation was achieved by the anodic oxidation of α-heteroatom-substituted organostannanes having a carbon–carbon double bond in an appropriate position,[6] but the corresponding intermolecular reaction was unsuccessful.

Organosilicon compounds are widely utilized as carbon nucleophiles. As shown in Table 1, the half-wave potentials for the oxidation of organosilicon compounds such as allylsilanes and silyl enol ethers are much more positive than those of α-heteroatom-substituted organostannanes.[7] Therefore, we reasoned that organosilicon compounds can be utilized as carbon nucleophiles in the electrochemical oxidation of α-heteroatom-substituted organostannanes; organostannanes are selectively oxidized to generate the carbocation intermediate **A**, which would react with organosilicon compounds (Scheme 1).[8] Therefore, we examined the anodic oxidation of α-heteroatom-substituted organostannanes in the presence of such organosilicon compounds as carbon nucleophiles, and found that the reaction proceeded smoothly to give the corrresponding coupling products.

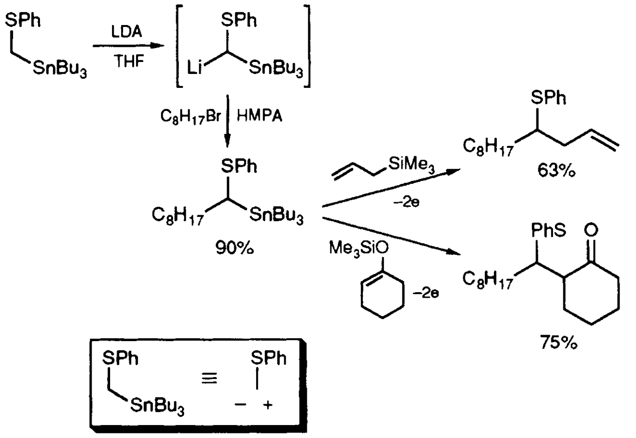
Typically, (menthyloxymethyl)tributylstannane (69 mg, 0.15 mmol), allyltrimethylsilane (86 mg, 0.76 mmol) dichloromethane (1.0 ml), Bu_4NBF_4 (80 mg, 0.24 mmol), and molecular sieves 4 Å (*ca.* 150 mg) were placed in an undivided cell equipped with a carbon-rod anode, a platinum-plate cathode, a Teflon stirrer bar, and an argon balloon. Constant electric current (10 mA) was applied under an atmosphere of argon. After 2.6 F mol^{-1} of electricity was consumed, aqueous work-up followed by flash chromatography yielded 4-menthyloxybut-1-ene (74%) (Table 2).

As the supporting electrolyte Bu_4NClO_4 and Bu_4NPF_6 were also effective. α-Alkoxystannanes, α-(*N*-methoxycarbonyl)-alkylaminostannanes and α-phenylthiostannanes were effective as α-heteroatom-substituted organostannanes. The reaction in the presence of silyl enol ethers as carbon nucleophiles also proceeds smoothly to give the corresponding coupling products, β-heteroatom-substituted ketones (Table 2).

Table 2 Electrooxidative coupling of α-heteroatom-substituted organostannanes and organosilicon compounds

Substrate	Nucleophile	Supporting electrolyte[a]	Electricity/ F mol^{-1}	Product	Yield (%)[b]
		A	2.6		74
		A	2.5		72
		A	2.2		68
		A	4.0		51
		A	2.0		71
		A	3.0		75
		A	2.4		69
		A	2.2		57
		B	2.6		63
		C	2.4		59
		A	3.0		75

[a] A: Bu_4NBF_4, B: Bu_4NClO_4, C: Bu_4NPF_6. [b] Isolated yields. [c] Men: menthyl.



Scheme 2

Synthetic utility of the present reaction is demonstrated by the following transformation (Scheme 2). (Phenylthiomethyl)-tributylstannane was readily deprotonated with lithium diisopropylamide (LDA)[9] and the resulting anion was treated with organic halides. The anodic oxidation of the alkylation product proceeded smoothly in the presence of allyltrimethylsilane or the silyl enol ether of cyclohexanone to give the coupling products. Therefore, both an electrophile and a nucleophile can be introduced onto the carbon adjacent to the sulfur atom.

We thank the Ministry of Education, Science, and Culture, Japan for a Grant-in-Aid for Scientific Research.

Received, 8th January 1993; Com. 3/00126A

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