Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8903155) for generous support of this work. We also thank the National Science Foundation for partial funding for the purchase of the Convex C210 computer used in this work.

Supplementary Material Available: Synthetic details for **2**, experimental IR data for **1**, and ab initio calculated geometries and vibrational frequencies for **1a**, **1b**, and **1c** (14 pages). Ordering information is given on any current masthead page.

Intramolecular Carbon–Carbon Bond Formation by the Anodic Oxidation of Unsaturated α-Stannyl Heteroatom Compounds. Synthesis of Fluorine-Containing Heterocyclic Compounds

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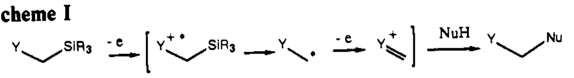
Although group 14 organometallic compounds are normally utilized as carbanion equivalents,[1,2] recent investigations reveal that they also serve as carbocation equivalents if one employs electrochemical oxidation.[3] For example, anodic oxidation of α-silyl ethers results in facile cleavage of the carbon–silicon bond and introduction of a nucleophile such as an alcohol onto the carbon (Scheme I). However, the introduction of carbon nucleophiles to form a new carbon–carbon bond by anodic oxidation of such compounds has remained an unexplored area of research.[4,5]

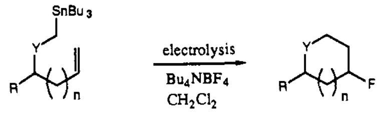
In this paper we wish to report that the anodic oxidation of α-stannyl ethers and carbamates containing carbon–carbon double bonds can lead to effective intramolecular carbon–carbon bond formation (Scheme II). A fluorine atom is introduced onto one of the original olefinic carbons in the cyclized product. The method outlined here is a new approach to both electrochemical carbon–carbon bond formation[6] and the synthesis of fluorine-containing compounds.[7,8]

Scheme I



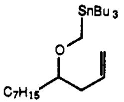
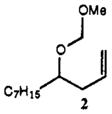
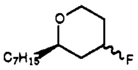
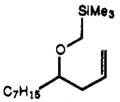
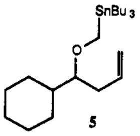
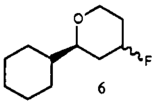
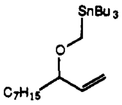
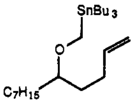
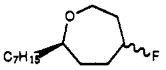
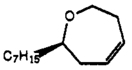
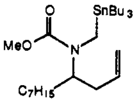
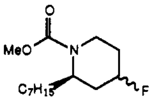
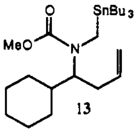
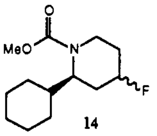
Y = R'O, R'S, R'NCO$_2$Me
NuH = R"OH, R"NHCO$_2$Me

Scheme II



Y = O, NCO$_2$Me
n = 1, 2

Table I. Intramolecular Carbon–Carbon Bond Formation by the Anodic Oxidation of Unsaturated α-Stannyl Ethers and Carbamates[a]

substrate	electrolyte	electricity (F/mol)	product	yield, %
 **1**	Bu_4NBF_4[b]	2.3	 **2**	93
	Bu_4NBF_4	3.1	 **3** (cis / trans = 2.8 : 1)	83
	Bu_4NPF_6	2.5	**3** (cis / trans = 1.2 : 1)	98
 **4**	Bu_4NBF_4	4.6	**3** (cis / trans = 1.2 : 1)	68
 **5**	Bu_4NBF_4	3.2	 **6** (cis / trans = 3 : 1)	95
 **7**	Bu_4NBF_4	3.2	complex mixture	
 **8**	Bu_4NBF_4	3.1	 **9**	61[c]
			 **10**	28
 **11**	Bu_4NBF_4	2.3	 **12** (cis / trans = 1.5 : 1)	70
 **13**	Bu_4NBF_4	2.0	 **14** (cis / trans = 3.1 : 1)	50

[a] The reactions were normally carried out with 0.25 mmol of the substrate. [b] Methanol was used as solvent. [c] A mixture of two stereoisomers (1.8:1).

We initially examined the anodic oxidation of α-stannyl ether **1** (Scheme III) because in the case of α-silyl ethers the radical intermediate generated by the first one-electron oxidation would be oxidized spontaneously on the surface of the anode (Scheme I). The oxidation potentials of carbon radicals are generally much

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[1] For example, (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: West Berlin, 1983.

[2] Organostannanes are also used as carbon radical equivalents. For example: Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.

[3] For example, (a) Yoshida, J.; Matsunaga, S.; Murata, T.; Isoe, S. *Tetrahedron* **1991**, *47*, 615–624. (b) Koizumi, T.; Fuchigami, T.; Nonaka, T. *Chem. Express* **1986**, *1*, 355–358. (c) Schaefer, H. J.; Hermeling, D.; Lange, K.-H. *Extended Abstracts*, Spring Meeting of the Electrochemical Society, May 6–11, 1984, Cincinnati, OH; p 441 and references cited therein.

[4] Carbon–carbon bond formation by the anodic oxidation of silyl enol ethers has been achieved: Schäfer, H. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 911–934.

[5] Carbon–carbon bond formation has been achieved by photoelectron-transfer reactions of organometallic compounds. See, for example: (a) Cho, I.-S.; Tu, C.-L.; Mariano, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 3594–3607. (b) Mizuno, K.; Nakanishi, K.; Otsuji, Y. *Chem. Lett.* **1988**, 1833–1836 and references cited therein. Oxidative carbon–carbon bond formation using thallium(III) trifluoroacetate has been reported: (c) Ochiai, M.; Arimoto, M.; Fujita, E. *Tetrahedron Lett.* **1981**, *22*, 4491–4494.

[6] Anodic oxidation: (a) Moeller, K. D.; Tinao, L. V. *J. Am. Chem. Soc.* **1992**, *114*, 1033–1041. (b) Hudson, C. M.; Marzabadi, M. R.; Moeller, K. D.; New, D. G. *J. Am. Chem. Soc.* **1991**, *113*, 7372–7385 and references cited therein. Cathodic reduction: (c) Amputch, M. A.; Little, R. D. *Tetrahedron* **1991**, *47*, 383–402. Lombardo, F.; Newmark, R. A.; Kariv-Miller, E. *J. Org. Chem.* **1991**, *56*, 2422–2427. Shono, T.; Kise, N.; Uematsu, N.; Morimoto, S.; Okazaki, E. *J. Org. Chem.* **1990**, *55*, 5037–5041 and references cited therein.

[7] Reviews, for example: (a) Welch, J. T. *Tetrahedron* **1987**, *43*, 3123–3197. (b) Gerstenberger, M. R. C.; Haas, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 647–667. (c) Schlosser, M. *Tetrahedron* **1978**, *34*, 3–17.

[8] Electrochemical fluorination, for example: (a) Fuchigami, T.; Shimojo, M.; Konno, A.; Nakagawa, K. *J. Org. Chem.* **1990**, *55*, 6074–6075. (b) Brigaud, T.; Laurent, E. *Tetrahedron Lett.* **1990**, *31*, 2287–2290 and references cited therein.

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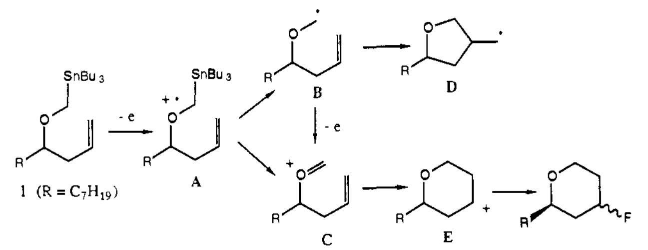
Scheme III



1 ($R = C_7H_{19}$)

less positive than those of α-silyl ethers. The oxidation potentials of α-stannyl ethers, however, are 0.5–0.7 V less positive than those of the corresponding α-silyl ethers.[9] Therefore, we reasoned that in the anodic oxidation of α-stannyl ethers the radical intermediate **B** might have a chance to cyclize before oxidation to the carbocation (radical cyclization). Other possibilities to be considered were that anodic oxidation of **B** might still be faster than cyclization or that the carbon–tin bond in **A** would be cleaved homolytically to give cation **C** directly. Thus generated, cation **C** would also have a chance to cyclize to give cation **E** (cation cyclization).[10] If the radical cyclization took place, then the five-membered-ring product would be formed (**B** → **D**), and if the cation cyclization took place, then the six-membered-ring product would be formed (**C** → **E**). Therefore, compound **1** seemed to be a suitable substrate for distinguishing between the radical and the cation cyclization pathways.

Although anodic oxidation of **1** in methanol gave the noncyclized acetal **2**, we found that switching the solvent to dichloromethane resulted in the facile formation of the six-membered-ring compound **3** (Table I).[11] The absence of the corresponding five-membered ring suggested that the cyclizations involved carbocation rather than radical intermediates.[12] To our surprise, the cyclized product contained a fluorine atom at one of the original olefinic carbons, indicating that fluoride ion from Bu_4NBF_4 attacked the cyclized cation **E** as a nucleophile.[13] Bu_4NPF_6 was also found to be effective as the fluoride source. Anodic oxidation of the corresponding α-silyl ether **4** also gave the cyclized product **3** under similar conditions, but the yield was lower and significant amounts of unidentified byproducts were formed.

The present method is generally applicable to endo cyclization to form six- and seven-membered rings (**1** → **3**, **5** → **6**, **8** → **9** + **10**). Endo cyclization to form a five-membered ring was not successful (**7**→). It is worth noting that α-stannyl carbamates also cyclized under similar conditions to give the corresponding fluorine-containing piperidine derivatives (**11** → **12**, **13** → **14**).

In summary, effective intramolecular carbon–carbon bond formation has been achieved by the anodic oxidation of unsaturated α-stannyl ethers and α-stannyl carbamates. The reactions also provide an efficient route to fluorine-containing compounds.[7,8] Studies concerning the reaction mechanism and synthetic applications are underway.

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

Supplementary Material Available: Listing of spectral data for the cyclized products (4 pages). Ordering information is given on any current masthead page.

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(9) Introduction of a silyl or stannyl group on the α-carbon of ethers results in a dramatic decrease in the oxidation potential. The effect of tin is larger than that of silicon. (a) Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962–1970. (b) Yoshida, J.; Ishichi, Y.; Nishiwaki, K.; Shiozawa, S.; Isoe, S. *Tetrahedron Lett.* **1992**, *33*, 2599–2602.

(10) Perron-Sierra, F.; Promo, M. A.; Martin, V. A.; Albizati, K. F. *J. Org. Chem.* **1991**, *56*, 6188–6199.

(11) In an undivided cell equipped with a carbon rod anode, a platinum plate cathode, a Teflon stir bar, and an argon balloon were placed compound **1** (119 mg, 0.25 mmol), dichloromethane (2.5 mL), Bu_4NBF_4 (201 mg, 0.61 mmol), and 4A molecular sieves (ca. 500 mg). A constant electric current of 5 mA was applied. After 3.1 faradays/mol of electricity was consumed, the aqueous workup followed by preparative TLC yielded compound **3** (83%, cis:trans = 2.8:1).

(12) Sometimes a heteroatom in the chain may also favor six-membered-ring formation in radical cyclization. See: Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: Oxford, 1986; p 147.

(13) For the formation of fluorine-containing compounds by nucleophilic reaction of BF_4^- or BF_3: (a) Faller, J. W.; Linebarrier, D. L. *Organometallics* **1990**, *9*, 3182–3184. (b) Wei, Z. Y.; Wang, D.; Li, J. S.; Chan, T. H. *J. Org. Chem.* **1989**, *54*, 5768–5774.

NMR Evidence for the Existence of a π-Accepting PMe_3 Ligand. Estimates of the Magnitude of π Effects in $WL(CO)_5$ Complexes

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While it is well established that alkylphosphite ligands function as relatively strong π electron acceptors in transition metal carbonyls,[2] the π bonding properties of the alkylphosphines remain poorly understood. The traditional view that they are moderate π acceptors[2] has been challenged by recent experiments inferring that these ligands can be π neutral or even, in some cases, net π electron donors.[3,4]

Unfortunately, Cotton–Kraihanzel (C–K) force constants,[5] classically used to monitor π bonding, are now known to depend upon both the σ and π components of the M–CO bond.[6] In contrast, it has been demonstrated that variations in the oxygen-17 quadrupole coupling constants (QCCs), $\chi(^{17}O)$, in multiply bonded systems[7,8] including metal carbonyls[9-11] reflect almost entirely changes in the π bond strength and are relatively insensitive to the σ bond component.

In order to assess the relative π acceptor capabilities of a typical alkylphosphine, we have performed a comparative NMR (^{17}O and

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(1) (a) Robert A. Welch Predoctoral Fellow. (b) Department of Chemistry, University of North Texas. (c) Center for Organometallic Research and Education, University of North Texas.

(2) (a) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole Publishing Co.: Monterey, CA, 1985. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(3) Angelici, R. J.; Malone, M. D. *Inorg. Chem.* **1967**, *6*, 1731.

(4) (a) Golovin, M. N.; Rahman, Md. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981. (b) Rahman, Md. M.; Liu, H.-Y.; Prock, A.; Giering, W. P. *Ibid.* **1987**, *6*, 650. (c) Rahman, Md. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Ibid.* **1989**, *8*, 1. (d) Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Ibid.* **1990**, *9*, 1758.

(5) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

(6) (a) Dobson, G. R. *Inorg. Chem.* **1965**, *4*, 1673. (b) Brown, T. L.; Darensbourg, D. J. *Ibid.* **1967**, *6*, 971. (c) Darensbourg, D. J.; Brown, T. L. *Ibid.* **1968**, *7*, 959. (d) Brown, D. A.; Rawlinson, R. M. *J. Chem. Soc. A* **1969**, 1530. (e) Fenske, R. F.; DeKock, R. L. *Inorg. Chem.* **1970**, *9*, 1053. (f) Fenske, R. F. *Pure Appl. Chem.* **1971**, *27*, 61.

(7) (a) Das, T. P.; Hahn, E. L. *Nuclear Quadrupole Resonance Spectroscopy*; Academic Press: New York, 1958. (b) Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants*; Academic Press: New York, 1969.

(8) (a) Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 2327. (b) Cheng, C. P.; Brown, T. L. *Ibid.* **1980**, *102*, 6418. (c) Bronsen, S. G. P.; Edmonds, D. T.; Poplett, J. J. *J. Magn. Reson.* **1981**, *45*, 451.

(9) (a) Aime, S.; Gobetto, R.; Osella, D.; Milone, L.; Hawkes, G. E.; Randall, E. W. *J. Chem. Soc., Chem. Commun.* **1983**, 794. (b) Hawkes, G. E.; Randall, E. W.; Aime, S.; Osella, D.; Elliot, J. E. *J. Chem. Soc., Dalton Trans.* **1984**, 279. (c) Aime, S.; Gobetto, R.; Osella, D.; Hawkes, G. E.; Randall, E. W. *Ibid.* **1984**, 1863. (d) Hawkes, G. E.; Randall, E. W.; Aime, S.; Gobetto, R. *J. Magn. Reson.* **1986**, *68*, 597. (e) Aime, S.; Botta, M.; Gobetto, R.; Osella, D. *J. Chem. Soc., Dalton Trans.* **1988**, 791.

(10) (a) Brownlee, R. T. C.; O'Connor, M. J.; Shehan, B. P.; Wedd, A. G. *J. Magn. Reson.* **1985**, *61*, 22. (b) Brownlee, R. T. C.; Shehan, B. P. *Ibid.* **1986**, *66*, 503. (c) Brownlee, R. T. C.; O'Connor, M. J.; Shehan, B. P.; Wedd, A. G. *Aust. J. Chem.* **1986**, *39*, 931.

(11) Wang, S. P.; Yuan, P.; Schwartz, M. *Inorg. Chem.* **1990**, *29*, 484.

0002-7863/92/1514-7595$03.00/0