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Anodic Cyclization of Unsaturated α-Stannyl Ethers. Termination by Bromide derived from Dibromomethane

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Anodic oxidation of unsaturated α-stannyl ethers in Bu_4NClO_4–CH_2Br_2 results in effective cyclization and the introduction of bromide into one of the original olefinic carbons; a mechanism involving the coupling between the cyclized carbocation and Br^- generated by cathodic reduction of CH_2Br_2 is suggested.

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The construction of cyclic systems is an important process in organic synthesis, and a variety of olefin cyclizations have been studied extensively.[1,2] Recently we have found that the anodic oxidation of α-stannyl ethers and carbamates containing carbon–carbon double bonds using Bu_4NBF_4 as supporting electrolyte leads to effective cyclization and the introduction of fluoride onto one of the original olefinic carbons (Scheme 1, Nu = F).[3] In this reaction the stannyl group functions as an 'electro-auxiliary' which activates organic molecules towards electrochemical oxidation and also controls the reaction pathways.[4] Fluoroborate ion acts both as the supporting electrolyte and the termination agent of olefin cyclization.

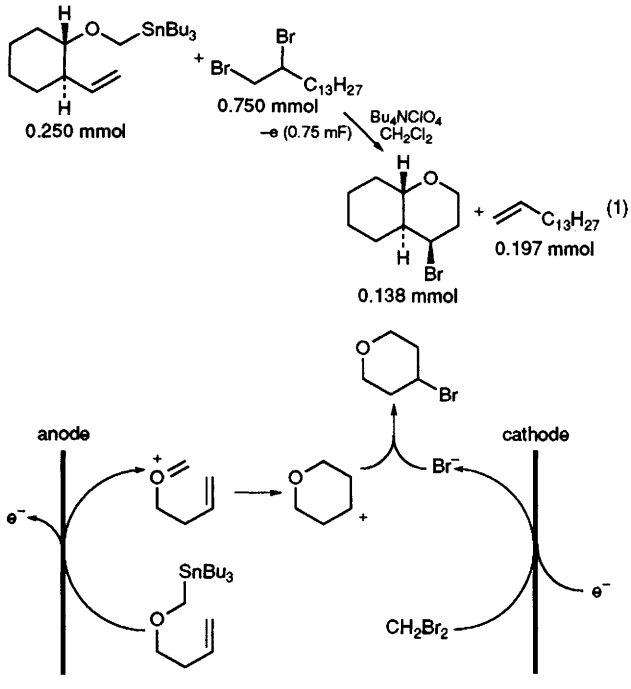
We have been interested in this termination by other nucleophiles such as bromide ion to obtain the cyclized bromides (Scheme 1, Nu = Br) because such compounds are versatile intermediates for further transformations.[5] Thus, we envisioned that the use of Br^- as the supporting electrolyte would lead to the formation of cyclized bromides. However, the reaction did not work. The electrolysis using Bu_4NBr led to selective oxidation of Br^- without affecting the organotin compounds, because the oxidation potential of Br^- is less positive than those for α-heteroatom-substituted organotin compounds.†

In order to solve this dilemma, we have devised a system in which bromide ions are generated by cathodic reduction in limited amounts during the course of the reaction, preventing the direct oxidation of bromide ions at the anode.

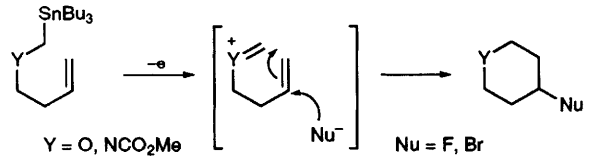
The reactions were carried out in an undivided cell equipped with a carbon rod anode and a platinum plate cathode, using a solution of Bu_4NClO_4 in CH_2Br_2. Aqueous work-up followed by flash chromatography yielded the cyclized bromides together with a small amount of cyclized olefins (Table 1). It is noteworthy that the reactions of *trans*-2-alkenyl-1-tributylstannylmethyloxycyclohexanes are highly selective. The reaction is specific in terms of the stereochemistry of the double bond in the side chain, and this stereospecificity can be explained in terms of a transition state, which arises from the chair-like conformation having two side-chains at equatorial positions[6] (Scheme 2). As for the stereochemistry at the carbon bearing bromide, only one isomer was obtained, suggesting axial attack of Br^- on the cyclized carbocation.‡[7]

In a divided cell, the formation of the cyclized bromide was greatly retarded and the cyclized olefins were obtained as major products, indicating that the cathodic reduction of CH_2Br_2 played an important role in this reaction. If the reaction proceeded by a radical mechanism involving the abstraction of Br from CH_2Br_2, the use of a divided cell would not affect the formation of the cyclized bromide. But this is not the case. Therefore, it is reasonable to consider that the reaction proceeds by a cationic mechanism involving the attack of Br^- generated by the cathodic reduction of CH_2Br_2 on the cyclized cation. Although the attempt to isolate carbon-containing products derived from the cathodic reduction of CH_2Br_2 was unsuccessful,[8] the reaction using 1,2-dibromopentadecane as the bromide source led to the formation of 1-pentadecene[9] together with the cyclized bromide (eqn. 1), indicating that the cathodic reduction of the dibromide takes place to produce Br^- during the course of the reaction.

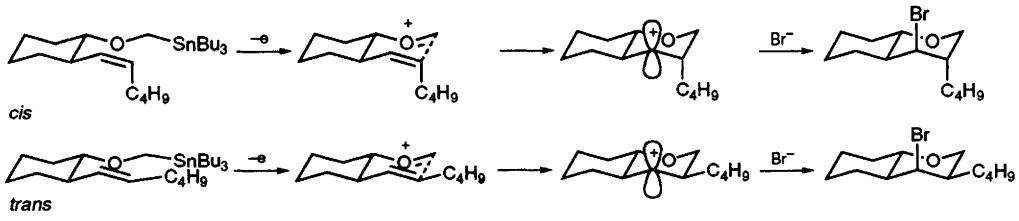
Thus, we may conclude that the present reaction is an



Scheme 3



Scheme 1



Scheme 2

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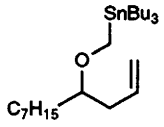
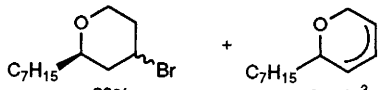
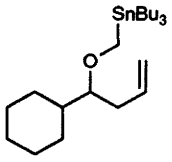
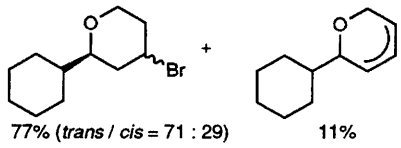
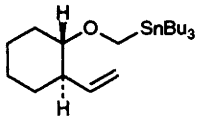
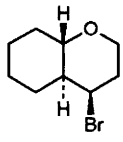
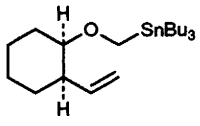
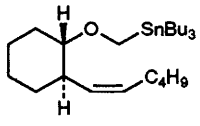
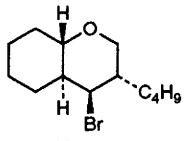
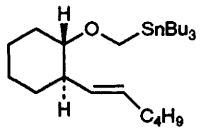
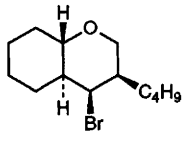
Table 1 Anodic cyclization of unsaturated α-stannyl ethers with CH_2Br_2[a]

Substrate	Electricity ($F\,mol^{-1}$)	Solvent	
	2.4	CH_2Br_2	 82% (*trans* / *cis* = 73 : 27) + 9% (Δ^3 : Δ^4 = 6 : 4)
			13% (almost *trans*) + 53% (Δ^3 : Δ^4 = 1 : 1)
			0% + 19% (Δ^3 : Δ^4 = 1 : 1)
	2.5	CH_2Br_2[b]	
	3.1	CH_2Br_2[c]	
	2.6	CH_2Br_2	 77% (*trans* / *cis* = 71 : 29) + 11%
	2.6	CH_2Br_2	 70%
	2.6	CH_2Br_2	complex mixture
	2.6	CH_2Br_2	 56%
	2.3	CH_2Br_2	 72%

a Reactions were normally carried out with 0.25 mmol of a substrate using 0.2 mol dm^{-3} of Bu_4NClO_4–CH_2Br_2 (2.5 ml) in an undivided cell equipped with a carbon rod anode and a platinum plate cathode under constant current conditions, unless otherwise state. *b* Reaction carried out in a two-compartment cell divided by sintered glass. *c* Reaction carried out in a two-compartment cell divided by Nafion 117 film.

example of the coupling between the carbocation generated by anodic oxidation of α-stannyl ethers followed by the cyclization and the introduction of Br^- generated by cathodic reduction of organic dihalides such as CH_2Br_2 (Scheme 3).

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Footnotes

† The half-wave oxidation potential of Et_4NBr is 0.70 V *vs.* Ag/AgCl, and that of α-stannyl ethers are around 1.2 V.

‡ According to the MM2 calculations,[10] the products are the thermodynamically less stable isomer with respect to the stereochemistry at the carbon bearing bromide, indicating that the stereoselectivity of the present reaction is determined kinetically.

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3 J. Yoshida, Y. Ishichi and S. Isoe, *J. Am. Chem. Soc.*, 1992, **114**, 7594.
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6 J. M. Barks, D. W. Knight and G. G. Weingarten, *J. Chem. Soc., Chem. Commun.*, 1994, 719.
7 If the addition across the carbon–carbon double bond occurs in an antiperiplanar fashion, the bromide group occupies the equatorial position. But this is not the case. Therefore, a stepwise addition involving axial attack of Br^- on the cyclized carbocation seems to be more plausible. See F. Perron-Sierra, M. A. Promo, V. A. Martin and K. F. Albizati, *J. Org. Chem.*, 1991, **56**, 6188.
8 For cathodic reduction of *gem*-polyhalides such as CCl_4 in the absence of proton donor, a mechanism involving carbene as an intermediate is proposed. See A. J. Fry, *Synthetic Organic Electrochemistry*, 2nd ed., Wiley, New York, 1989, pp. 148–149.
9 Cathodic reduction of *vic*-dibromides is known to give the corresponding olefins. For example, U. Husstedt and H. J. Schäfer, *Tetrahedron Lett.*, 1981, **22**, 623.
10 MM2(87). N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127.

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