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

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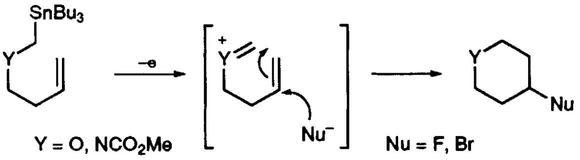
Anodic oxidation of unsaturated α-stannyl ethers in $Bu_4NClO_4$–$CH_2Br_2$ results in effective cyclization and the introduction of bromide into one of the original olefinic carbons; a mechanism involving the coupling between the cyclized carbocation and $Br^-$ generated by cathodic reduction of $CH_2Br_2$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

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.

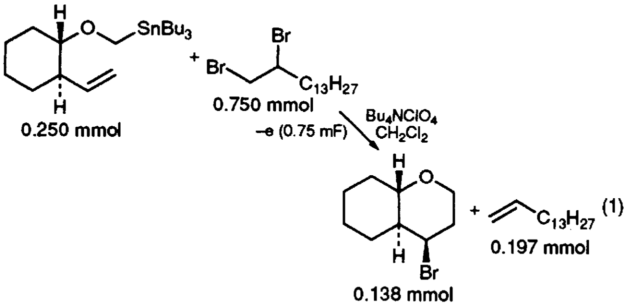
The reactions were carried out in an undivided cell equipped with a carbon rod anode and a platinum plate cathode, using a solution of $Bu_4NClO_4$ in $CH_2Br_2$. Aqueous work-up followed by flash chromatography yielded the cyclized bromides together with a small amount of cyclized olefins (Table 1). 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]

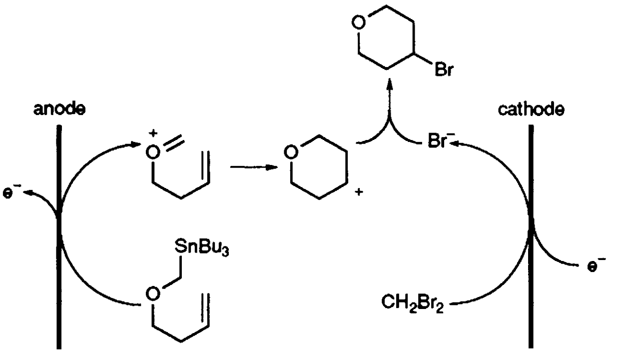


Scheme 1

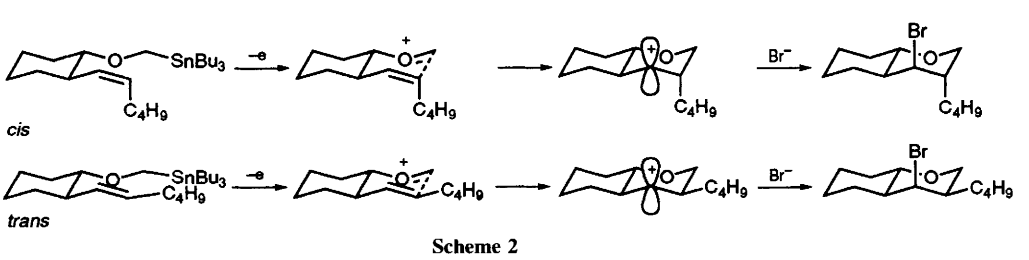
In a divided cell, the formation of the cyclized bromide was greatly retarded and the cyclized olefins were obtained as major products, indicating that the cathodic reduction of $CH_2Br_2$ played an important role in this reaction. If the reaction proceeded by a radical mechanism involving the abstraction 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



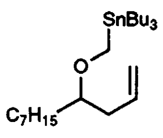
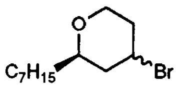
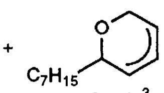
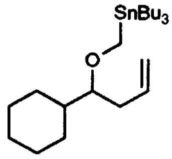
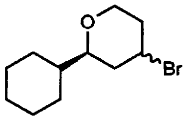
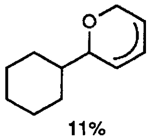
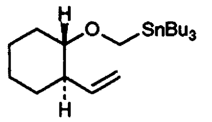
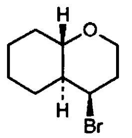
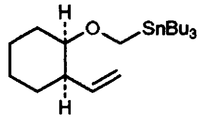
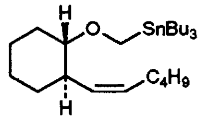
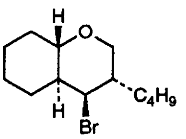
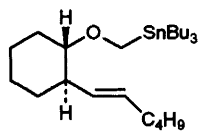
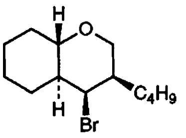


Scheme 3



Scheme 2

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

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

## References

1 For example, W. S. Johnson, *Angew. Chem.*, 1976, **88**, 33.

2 Anodic Olefin cyclization: for example, T. Shono, I. Nishiguchi, S. Kashimura and M. Okawa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2181; G. W. Morrow, Y. Chen and J. S. Swenton, *Tetrahedron*, 1991, **47**, 655; K. D. Moeller and L. V. Tinao, *J. Am. Chem. Soc.*, 1992, **114**, 1033 and references cited therein.

3 J. Yoshida, Y. Ishichi and S. Isoe, *J. Am. Chem. Soc.*, 1992, **114**, 7594.

4 Tin and silicon have recently been used as effective 'electro-auxiliaries' in electro-organic chemistry. For examples see J. Yoshida and S. Isoe, *Tetrahedron Lett.*, 1987, **28**, 6621; J. Yoshida, M. Itoh and S. Isoe, *J. Chem. Soc., Chem. Commun.*, 1993, 547; K. Suda, K. Hotoda, J. Watanabe, K. Shiozawa and T. Takanami, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1283.

5 Nucleophile (such as $Br^-$)-promoted electrophilic cyclization reactions of alkynes has been reported: L. E. Overman and M. J. Sharp, *J. Am. Chem. Soc.*, 1988, **110**, 612. Formic acid-mediated cyclizations of alkenes has also been reported: P. M. Esch, R. F. de Boer, H. Hiemstra, I. Boska and W. N. Speckamp, *Tetrahedron*, 1991, **47**, 4063.

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.