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Cyclization of Alkene-Containing Tetraalkylstannanes

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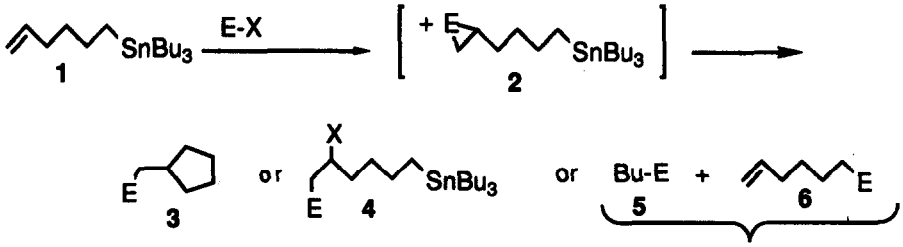
Abstract: We have discovered a novel cyclization reaction, achieved through selective electrophilic cleavage of an organotin compound containing remote alkene functionality. The reaction has proven to be quite general with respect to a variety of substitution patterns.

In order to further enhance the synthetic utility of our recently-discovered cycloaddition reaction where allylstannanes and α,β–unsaturated acyliron complexes are combined to produce tributyltin-substituted cyclopentane derivatives,[1] we have embarked upon a program to develop new carbon-tin bond cleavage reactions. We have developed a method for conversion of a tributyltin group at a secondary carbon atom to the corresponding alcohol with retention of configuration at carbon.[2] Carbon-tin bond cleavage reactions which lead to direct formation of carbon-carbon bonds are potentially more useful processes. The intramolecular reaction of tetraalkylstannanes with carbocations can often lead to three-[3] or five-membered[4] carbocycle formation in very high yield. Five-membered ring-forming processes are usually initiated from oxygen-containing carbocation precursors, and thus are not compatible with the reaction in reference 1. The reaction of 5-hexenyltributyltin with halogens and pseudohalogens produces cyclization products only when the counterion is very non-nucleophilic (Scheme 1).[5] The scope and limitations of this cyclization reaction with respect to alkene and tethering-chain substitution pattern are reported herein.

SCHEME 1. Reaction of 5-Hexenyltributyltin with Electrophiles (E^+X^-).

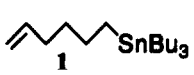
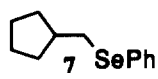
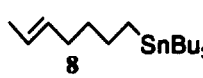
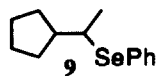
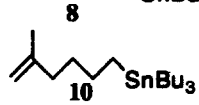
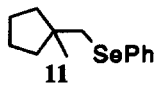
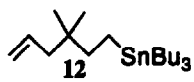
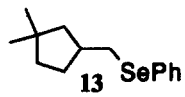
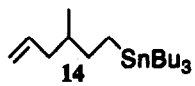
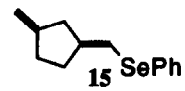
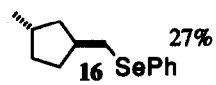
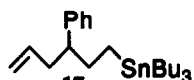
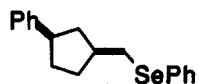
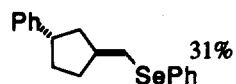
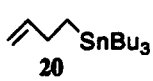
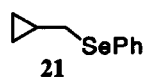


From Direct Cleavage of the C-Sn Bonds

A variety of alkene-containing tetraalkylstannanes have been prepared and examined for their reactivity toward N-phenylselenophthalimide (NPSP) and tin tetrachloride at -78 °C in dichloromethane. This combination of reagents was reported to produce the highest yield of cyclization product when reacted with stannane **1**.[5] In the Table, the yield and identity of the cyclization products from this reaction are reported. The cyclization reaction proceeds with monosubstituted (Entries A, D, E, and F), 1,1-disubstituted (Entry C), and 1,2-disubstituted alkenes (Entry B). Three-

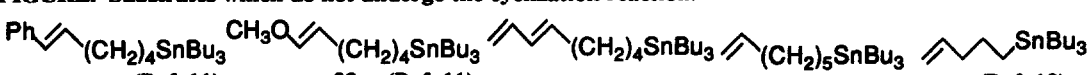
membered rings can also be produced from this reaction (Entry G). Listed in the Figure are some substrates which are not suitable for the reaction. This cyclization reaction is apparently restricted to the formation of three- and five-membered rings, since substrates that would lead to other ring sizes (e.g. **25**, **26**) do not undergo the cyclization reaction. Also, substrates such as **22-24**, where the most electrophilic carbon of the episelenonium cation intermediate is six carbons away, do not undergo the cycloaddition reaction. Note that in compound **2**, the more electrophilic carbon[6] is five carbons away and cyclization proceeds readily. Phenylselenium chloride double bond addition products are sometimes observed when the cyclization fails or proceeds in low yield.

TABLE. Reaction of Alkenes Containing Remote Tributyltin Groups with NPSP/$SnCl_4$.[a]

ENTRY	STANNANE		PRODUCT(S) & YIELD	
A	 **1**	(Ref. 10)	 **7**	99%
B	 **8**	(Ref. 11)	 **9**	93%
C	 **10**	(Ref. 12)	 **11**	49%
D	 **12**	(Ref. 13)	 **13**	66%
E	 **14**	(Ref. 13)	 **15**	52%
			 **16**	27%
F	 **17**	(Ref. 13)	 **18**	62%
			 **19**	31%
G	 **20**	(Ref. 10)	 **21**	71%

[a] For a procedure, see reference 5.

FIGURE. Substrates which do not undergo the cyclization reaction.

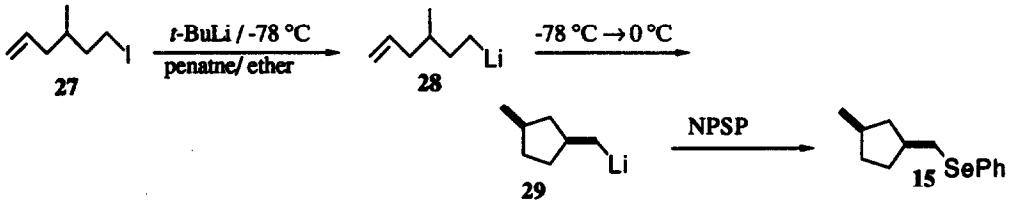


22 (Ref. 11) **23** (Ref. 11) **24** (Ref. 11) **25** (Ref. 10) **26** (Ref. 10)

The reaction proceeds with only a modest degree of stereoselectivity as can be seen in Entries E and F of the Table. The major stereoisomer in Entry E is assigned as the cis isomer via authentic synthesis. Conversion of iodide **27** (Scheme 2) to organolithium derivative **28**, followed by warming to 25 °C is known to produce mostly the cis organolithium derivative **29**. Treatment of **29** with NPSP provided selenides **15** and **16** in a 10:1 mixture. The major isomer from the reaction in Scheme 2 is identical to the major isomer obtained from NPSP-induced cyclization of

stannane **14**. The stereoselectivity in selenium-induced cyclization of alkene-stannanes is noticeably lower than that obtained in the anion cyclization[7] or the recently-reported organotitanium-mediated cyclization,[8] but similar to that reported for radical cyclizations.[9] Since the cation intermediate of the alkene-stannane cyclization is very highly electrophilic, then the transition state is probably very reactant-like, thus the half-chair transition state proposed by Bailey is less important in our reaction. Interestingly, attempts to prepare compounds **18-19** by the anion cyclization route have not been successful.

SCHEME 2. Authentic Synthesis-Stereochemical Assignment of Compound 15.



27 **28** **29** **15**

(Ref. 7)

Since 5-hexenyllithium derivatives (e.g. **28**, Scheme 2) used in the preparation 5-hexenylstannanes undergo direct cyclization at 20 °C, an obvious question is: what advantages does the organotin method offer? Advantages of this method include successful cyclization reactions with 1,2-disubstituted alkenes, successful cyclization at -78 °C, and successful cyclization reactions when both three- and five-membered rings are formed. Although similar three-membered ring-forming cyclization reactions of 4-stannyl-1-butenes are well-documented,[3g,h] only these conditions allow for the reaction to proceed at -78 °C. Further evaluation of other cyclization initiators is presently in progress.

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References:

1. Herndon, J.W.; Wu, C.; Harp, J.J. *Organometallics* **1990**, *9*, 3157-71.

2. Herndon, J.W.; Wu, C. *Tetrahedron Lett.*, **1989**, *30*, 6461-64.

3. For three-membered ring-forming reactions, see a. Plamondon, L.; Wuest, J.D. *J. Org. Chem.* **1991**, *56*, 2066-2076. b. Plamondon, L.; Wuest, J.D. *J. Org. Chem.* **1991**, *56*, 2076-2081. c. Sato, T. *Synthesis* **1990**, 259-270. d. Sato, T.; Watanabe, T.; Hayata, T.; Tsuki, T. *Tetrahedron* **1989**, *45*, 6401-6408. e. Johnson, C.R.; Kadow, J.F.; *J. Org. Chem.* **1987**, *52*, 1493-1500. f. Fleming, I.; Urch, C.J. *J. Organometal. Chem.* **1985**, *285*, 173-191. g. Peterson, D.J.; Robbins, M.D. *Tetrahedron Lett.* **1972**, 2135-2138. h. Nicolau, K.C.; Claremon, D.A.; Barnette, W.E.; Seitz, W.P. *J. Am. Chem. Soc.* **1979**, *101*, 3704-3706.

4. For five-membered ring-forming reactions, see a. Sato, T.; Haramura, M.; Taka, N. *Tetrahedron Lett.* **1989**, *30*, 4983-4984. b. Lee, T.V.; Ellis, K.L. *Tetrahedron Lett.* **1989**, *30*, 3555-3556. c. MacDonald, T.L.; Delahunty, C.M.; Mead, K.; O'Dell, D.E. *Tetrahedron Lett.* **1989**, *30*, 1473-1476. d. Fleming, I.; Rowley, M. *Tetrahedron* **1986**, *42*, 3181-3198.

5. Herndon, J.W.; Harp, J.J. *J. Organometal. Chem.* **1990**, *393*, C1-C5.

6. Garratt, D.G.; Schmid, G.H. *Can. J. Chem.* **1974**, *52*, 3599-3606. For a review of this subject, see Back, T.G. In *Organoselenium Chemistry*; Liotta, D. Ed; John Wiley and Sons: New York, 1987; pp 56-99.

7. Bailey, W.F.; Khanolkar, A.D.; Gavaskar, K.; Ovasaka, T.V.; Rossi, K.; Thiel, Y.; Wiberg, K.B. *J. Am. Chem. Soc.* **1991**, *113*, 5720-5727.

8. Young, J.R.; Stille, J.R. *Organometallics* **1990**, *9*, 3022-3025.

9. Beckwith, A.L.J.; Lawrence, T.; Serelis, A.K. *J. Chem. Soc., Chem. Commun.* **1980**, 484-485.

10. Prepared by reaction of commercially-available bromoalkenes with magnesium, then tributyltin chloride.

11. Prepared from compound **1** by oxidative cleavage (OsO_4 / $NaIO_4$) followed by an appropriate Wittig reaction.

12. Prepared from readily-available 5-oxohexanenitrile. Ketone protection (ethylene glycol, acid), nitrile hydrolysis (aq. NaOH), reduction ($LiAlH_4$), conversion to the iodide (methanesulfonyl chloride, then sodium iodide), conversion to the stannane (*t*-BuLi, -78 °C, pentane/ ether solution,[14] then tributyltin chloride), deprotection (aqueous acid) and Wittig reaction afforded stannane **11**. A more straightforward route was abandoned because attempted conversion of 6-mesyloxy-2-methyl-1-hexene to the iodide resulted in partial isomerization of the alkene. These isomers could not be separated under any conditions.

13. Prepared using the Santelli reaction.[15] An appropriately-substituted α,β–unsaturated acyl cyanide was treated with allyltrimethylsilane, to give after hydrolysis the δ,ε–unsaturated carboxylic acid. Reduction ($LiAlH_4$), conversion to the iodide (methanesulfonyl chloride, then sodium iodide), conversion to the organolithium reagent (*t*-BuLi, -78 °C, pentane/ ether solution),[14] and treatment with tributyltin chloride afforded the stannane.

14. a. Bailey, W.F.; Punzalan, E.R. *J. Org. Chem.* **1990**, *55*, 5404-5406. b. Negishi, E.; Swanson, D.R.; Rouset, C.J. *J. Org. Chem.* **1990**, *55*, 5406-5409.

15. Santelli, M.; El Abed, D.; Jellal, A. *J. Org. Chem.* **1986**, *51*, 1199-1206.

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