Journal of Organometallic Chemistry, 393 (1990) C1–C5
Elsevier Sequoia S.A., Lausanne
JOM 21109PC

Preliminary communication

Reaction of 5-hexenyltributyltin with pseudohalogens: cyclization vs. double bond addition

James W. Herndon * and Jill J. Harp

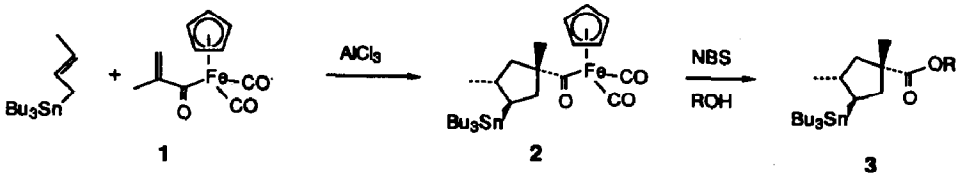
Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742 (U.S.A.)

(Received March 6th, 1990)

Abstract

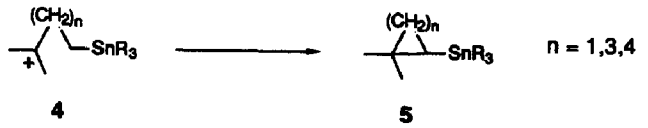
Reaction of 5-hexenyltributyltin with pseudohalogen electrophiles leads to either double bond addition products or cyclization products. When electrophiles containing non-nucleophilic counterions are used, predominately cyclization products are formed.

We recently reported that the reaction between allylstannanes and α,β-unsaturated acyliron complexes under Lewis acid catalysis leads to the cyclopentane derivative **2** with a high degree of stereoselectivity [1] (Scheme 1). The acyliron functionality in compound **2** is easily converted to the corresponding ester. The tetraalkyltin group is considerably more difficult to cleave, and since two types of alkyl groups are present at tin in compound **3** there is also a potential chemoselectivity problem. Methods have been reported to convert the tributyltin group in compounds such as **3** into ketones [2] and alcohols [3], and carbon–tin bonds



1 2 3

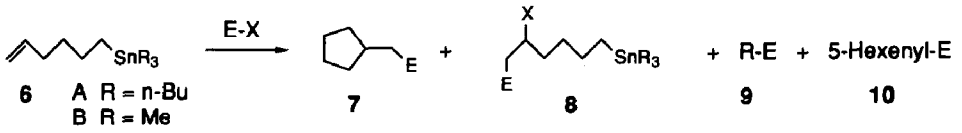
Scheme 1



4 5

Scheme 2

0022-328X/90/$03.50



Scheme 3

undergo selective intramolecular cleavage reactions with carbocations (Scheme 2). Previous researchers have shown that homoallylic stannanes and γ-stannyl alcohols are easily converted to cyclopropane derivatives once a carbocation is generated at the γ-position [4]. Organostannanes containing enone, α,β-unsaturated acetal, or carbonyl functionality at appropriate positions can be cleaved selectively upon treatment with Lewis acids to effect carbocyclization into five- or six-membered ring systems [5]. In order to use the reaction in Scheme 1 for the possible synthesis of polyquinane compounds [6], we sought a method for the cleavage of the carbon–tin bond in such a way that a new carbon–carbon bond and a five-membered ring might be formed simultaneously. Since the [3 + 2] cycloaddition reaction is not compatible with oxygen functionality, the reaction in ref. 5 does not appear to be a practical solution to this problem. We therefore undertook an examination of the reaction of electrophiles with hexenyltributyltin. Herein we report our initial investigations of this reaction.

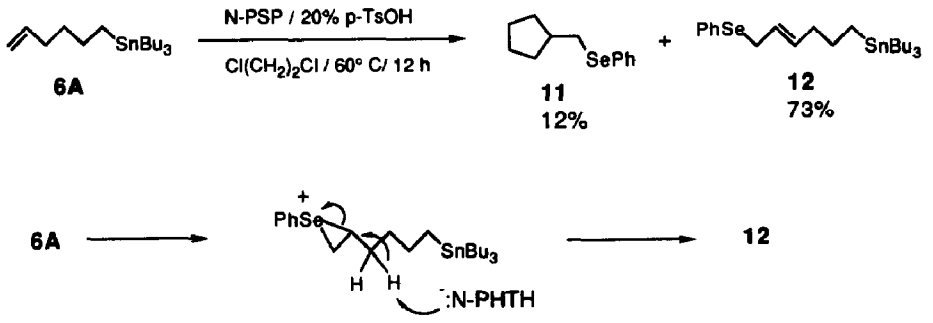
The initial studies were performed on compounds **6A** and **B**. In compound **6**, there are three places where electrophilic attack can occur: the R–tin bond, the hexenyl–tin bond or the double bond (Scheme 3). As can be seen in Table 1, electrophilic attack occurred predominately at the double bond, and in entries 1–4 the double bond addition product **8** was the major product of the reaction. When electrophiles were used which did not form stable double bond addition products (entries 6–8), electrophilic cleavage of a carbon–tin bond appeared to be the predominate mode of attack, and compounds **9** and **10** were the major products of the reaction. A comparison of entries 1 and 2 or 6 and 7 revealed that the methyl–tin bond was more susceptible to electrophilic cleavage than the butyl–tin bond. In the reaction mixture of entry 1, the methyl group was cleaved selectively in

Table 1

Reaction of compound **6** with electrophiles [a]

Entry	R	E–X	%7	%8	%9 and 10
1	Me	Br–Br	0	83	17 [b]
2	Bu	Br–Br	0	100	0
3	Me	PhSe–Cl	0	100	0
4	Bu	PhSe–Cl	0	100	0
5	Bu	I–Cl	2	25	73 [c]
6	Me	I–I	0	23	77 [d]
7	Bu	I–I	0	46	54 [c]
8	Bu	AcOHg–OAc	0	0	100 [e]

[a] The percentage of each compound was determined by ^{1}H NMR integration of the complete reaction mixture since the CH_2E protons have different chemical shifts and splitting patterns and can be integrated separately for compounds **7** and **8**, and **9** and **10** if R = CH_3; $CDCl_3$ was the solvent for the reaction. [b] Only **9** was obtained. [c] The relative amounts of **9** and **10** could not be determined. [d] The ratio of **9**:**10** was 4:1. [e] The ratio of **9**:**10** was 3:1.



Scheme 4

the presence of the 5-hexenyl group [7]. Cyclization to form the five-membered ring compound **7** is a very minor reaction pathway. The preponderance of double bond addition product (**8**) over cyclization products (**7**) is presumably due to the greater nucleophilicity of the counterion of the electrophile relative to the carbon–tin bond.

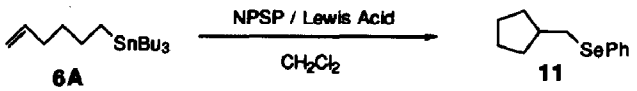
Next, the reaction of compound **6A** was examined with electrophiles having less nucleophilic counterions. Addition of silver salts to the reaction mixtures in entries 1, 2, and 4 unfortunately did not lead to an increase in the yield of cyclization products, perhaps due to side reactions at tin. The combination of *N*-phenylselenophthalimide (NPSP) and (5–10 mol%) *p*-toluenesulfonic acid had been reported to effect the conversion of 3-butenyltrimethylstannane to cyclopropylmethyl phenyl selenide at 25 °C [4a]. Compound **6A** did not react with this combination of reagents at 25 °C, but upon heating the solution to 60 °C (1,2-dichloroethane solvent) a mixture of two new compounds (**11** and **12**) was obtained (Scheme 4) [8*]. Presumably, the unwanted allylic selenide arose from a β-elimination from the bridging selenonium ion. This process was suppressed by the addition of more *p*-toluenesulfonic acid. When a stoichiometric amount of acid catalyst was used in the reaction of NPSP and stannane **6**, only the cyclization product **11** was obtained in 26% yield.

Although we had discovered a method to effect the desired cyclization reaction, the yields were not satisfactory, and the conditions required for this cyclization were very brutal. The formation of **11** was considerably more difficult than the formation of the three-membered ring compound, which cyclized in high yield at 25 °C. In order to further increase the electrophilicity of NPSP, the use of Lewis acids to effect the cyclization reaction was examined [9]. When titanium tetrachloride was substituted for *p*-toluenesulfonic acid, the cyclization reaction proceeded at −78 °C, and gave compound **11** in 56% yield along with butyl phenyl selenide in 8% yield. Butyl phenyl selenide results from a secondary cleavage reaction of a butyl group when a slight excess of NPSP/$TiCl_4$ was employed, and was not a competing process since when compound **6a** was used in excess no butyl phenyl selenide was formed. The reaction has been examined with a variety of Lewis acid catalysts (Table 2). Tin tetrachloride appeared to be the optimal catalyst, giving compound **11** in 98% yield. Boron trifluoride etherate was not an efficient catalyst for the reaction at −78 °C, but the cyclization reaction did proceed to completion when the

* Reference number with asterisk indicates a note in the list of references.

Table 2

Reaction of compound **6a** with NPSP and Lewis acids [a]



6A **11**

Entry	Lewis acid	Temperature (°C)	Time [b] (h)	Yield **11** [c] (%)
1	$TiCl_4$	−78	1	56
2	$SnCl_4$	−78	1	98
3	BF_3OEt_2	−78	2	35 [d]
4	$EtAlCl_2$	−78	1	34 [e]
5	*p*-TsOH	60	0.5	26

[a] For a procedure, see ref. 10 *. [b] The reaction was allowed to proceed to completion unless otherwise noted. [c] Actual yields. [d] The reaction had not gone to completion. [e] EtSePh was also obtained in 35% yield.

reaction was performed at 0 °C. When ethylaluminum dichloride was used as the catalyst, ethyl phenyl selenide formed as a byproduct, presumably from electrophilic cleavage of the carbon–aluminum bond. If any trace of halide ion or water was present as a contaminant, double bond addition products (**8**) began to appear. When less than stoichiometric amounts of Lewis acids were used, the cyclization reaction did not go to completion.

In summary, we have discovered a potential method to effect carbocyclization using tetraalkylstannanes containing an unactivated alkene five carbons away. The reaction is complementary to the recently discovered conversion of 5-hexenyllithium reagents to cyclopentylmethyllithium derivatives [11], and to the reactions in ref. 5. We are presently investigating the scope and limitations of this novel ring-forming reaction.

Acknowledgements. We thank the National Institutes of Health (GM-40777) and the General Research Board of the University of Maryland for support of this research, and the graduate school of the University of Maryland for a fellowship to Jill Harp. We thank Ms. Sung Ko for experimental assistance during the early stages of this project.

References and notes

1 J.W. Herndon, J. Am. Chem. Soc., 109 (1987) 3165; (b) J.W. Herndon and C. Wu, Tetrahedron Lett., 30 (1989) 5745.
2 W.C. Still, J. Am. Chem. Soc., 99 (1977) 4836.
3 (a) J.W. Herndon and C. Wu, Tetrahedron Lett., 30 (1989) 6461; (b) S. Ochiai, S. Iwaki, T. Ukita, Y. Matsuura, M. Shiro and Y. Nagao, J. Am. Chem. Soc., 110 (1988) 4606.
4 (a) K.C. Nicolau, D.A. Claremon, W.E. Barnette and S.P. Seitz, J. Am. Chem. Soc., 101 (1979) 3704; (b) D.J. Peterson and M.D. Robbins, Tetrahedron Lett., (1972) 2135; (c) I. Fleming and C.J. Urch, Tetrahedron Lett., 24 (1983) 4591; (d) C.R. Johnson and J.F. Kadow, J. Org. Chem., 52 (1988) 1493.
5 For leading references, see T.L. MacDonald, C.M. Delahunty, K. Mead and D.E. O'Dell, Tetrahedron Lett., 30 (1989) 1473.
6 L.A. Paquette and A.M. Doherty, Polyquinane Chemistry, Springer Verlag, Berlin, 1987.
7 S. Boué, M. Gielen and J. Nasielski, J. Organomet. Chem., 9 (1967) 443.
8 A solution of stannane **6a** (0.100 g, 0.27 mmol), *N*-phenylselenophthalimide (0.121 g, 0.4 mmol) and *p*-toluenesulfonic acid (0.010 g, 0.05 mmol) in 1,2-dichloroethane (0.5 mL) was heated to reflux under

a nitrogen atmosphere for 12 h. The solution was cooled to room temperature and the solvent removed on a rotary evaporator. Purification was achieved by flash chromatography on silica gel using hexane as the eluent; two fractions were collected. The less polar fraction was a yellow liquid, identified as compound **12** (0.103 g, 73%, 4:1 *trans:cis* mixture). ^{1}H NMR ($CDCl_3$): major isomer, δ 3.44 (d, 1.6 H, $J = 7.3$ Hz); minor isomer, δ 3.50 (d, 0.4 H, $J = 8.0$ Hz); the following peaks appeared in both isomers, 7.14–7.56 (m, 5H), 5.29–5.65 (m, 2H), 1.87–1.98 (m, 2H), 1.20–1.54 (m, 16H), 0.67–0.98 (m, 15H); ^{13}C NMR ($CDCl_3$): 133.7, 133.6, 130.5, 129.8, 128.9, 127.0, 126.2, 125.3, 37.0, 31.8, 30.2, 29.5, 29.3, 27.4, 26.9, 13.7, 8.9, 8.8; IR (neat): 3075 (m), 3025 (m), 2960 (s), 2925 (s), 2850, (s), 1575 (w), 1440 (m), 1115 (m), 1080 (m), 1025 (m), 745 (m), 690 (m) cm^{-1}. MS (CI): 531 ($M+1$, 1%), 473 (96%), 472 (45%), 471 (100%), 470 (52%), 469 (77%), 389 (49%), 315 (44%), 179 (46%), 177 (48%). HRMS (CI): calcd for $C_{24}H_{43}SeSn$, 531.1552; found, 531.1530. The more polar fraction was a colorless liquid, identified as compound **11** (0.0078 g, 12%). ^{1}H NMR ($CDCl_3$): δ 7.23–7.58 (m, 5H); 2.94 (d, 2H, $J = 7.3$ Hz); 2.13 (quintet, 1H, $J = 7.3$ Hz): 1.04–2.03 (m, 8H); ^{13}C NMR ($CDCl_3$): 132.4, 128.9, 126.5, 135.1, 40.4, 34.6, 33.1, 25.3; IR (neat): 3000(w), 2950(s), 2870(s), 1580(m), 1480(s), 1440(s), 1120(w), 733(s), 690(m) cm^{-1}. MS (CI): 240 (M, 16%), 158 (66%), 157 (24%), 156 (34%), 155 (21%), 83 (39%), 78 (26%), 77 (38%), 55 (100%), 51 (24%); HRMS (CI) calcd for $C_{12}H_{16}Se$, 240.0417; found, 240.0405.

9 S.V. Ley, B. Lygo, H. Molines and J.A. Morton, J. Chem. Soc., Chem. Commun., (1982) 1251.

10 To a solution of *N*-phenylselenophthalimide [4a] (0.041 g, 0.014 mmol) in dichloromethane (0.5 mL) under nitrogen at −78°C was added tin tetrachloride (0.14 mL of a 1 *M* solution in dichloromethane, 0.14 mmol). The mixture was stirred for 1 min at −78°C and a solution of compound **6a** (0.050 g, 0.13 mmol) in dichloromethane (0.1 mL) was added. The mixture was stirred at −78°C for 1 h, and then filtered through alumina and washed with hexane. After the solvent was removed on a rotary evaporator, the residue was purified by flash chromatography on silica gel using hexane as the eluent. After removal of the solvent, a colorless oil (0.031 g, 98%) identified as compound **11** was obtained. The spectral data were identical to those reported in ref. 8.

11 For leading references, see: W.F. Bailey, T.V. Ovaska and T.K. Leipert, Tetrahedron Lett., 30 (1989) 3901.