Tetrahedron Letters,Vol.30,No.52,pp 7349-7352,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

ON THE 1,3-ISOMERIZATION OF NONRACEMIC α-(ALKOXY)ALLYLSTANNANES

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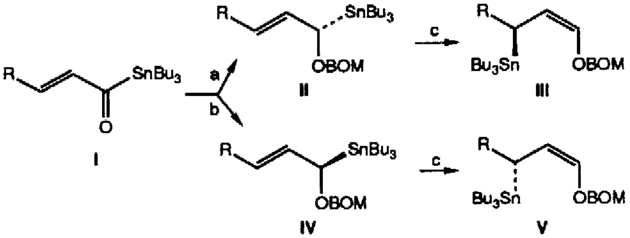
Summary: $BF_3 \cdot OEt_2$ promoted 1,3-isomerization of α-(alkoxy)allylstannanes to γ-(alkoxy)allylstannanes has been shown to proceed by an intermolecular anti S_E' process. A pathway involving pentacoordinated stannate intermediates is proposed.

In recent years allylstannanes have assumed an important role as reagents for organic synthesis.[1] We recently described a facile and stereospecific isomerization of nonracemic α-(alkoxy)allylstannanes to γ-(alkoxy)allylstannanes (eq. 1).[2] The ready availability of these nonracemic allylstannanes opens up new avenues of synthetic applications allowing, for example, the possibility of reagent as well as substrate controlled addition reactions in stereodirected synthesis.[3] Although in the case of eq. (1) it was not possible to directly assign absolute configuration to the rearranged stannanes III and V, their subsequent reactions with aldehydes under Lewis acid and thermal conditions were consistent with those depicted.[2,4] Accordingly, we surmized that the 1,3-stannyl migration must take place by an *anti* pathway in these systems. We now report additional observations which directly bear on this conclusion.

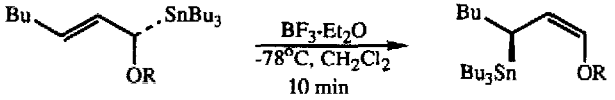


(1)

(a) (R)-(+)-BINAL-H, THF; (b) $LiAlH_4$-Chirald, THF; (c) $BF_3 \cdot Et_2O$, CH_2Cl_2, -78 °C

The reaction pathway for $BF_3 \cdot OEt_2$ promoted isomerization of allylstannanes has proved to be an enigma. Low temperature ^{13}C NMR data are "consistent with a rapid 1,3-shift by a process which labilizes the allyls for bimolecular exchange."[5] Because an intramolecular *anti* 1,3-migration (antarafacial process) is highly disfavored on steric grounds we felt that the aforementioned 1,3-shift process was most likely intermolecular.[9] Support for this conclusion was obtained from the experiments summarized in Table I. These studies also showed the reaction to be catalytic in $BF_3 \cdot OEt_2$ (entries 6 and 7).

Table I. Concentration Effects on the 1,3-Isomerization of α-(Alkoxy)allylstannanes



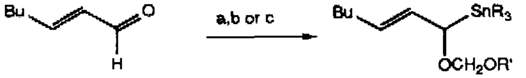
1 R = $PhCH_2OCH_2$
2 R = $MeOCH_2$

3 R = $PhCH_2OCH_2$
4 R = $MeOCH_2$

		concentration (*M*)		
entry	*stannane*	*stannane*	BF_3•OEt_2	*% reaction*
1	**1**	0.1	0.1	100
2	**1**	0.01	0.01	25
3	**2**	0.02	0.02	99
4	**2**	0.002	0.002	34
5	**2**	0.002	0.001	13
6	**2**	0.1	0.05	99[a]
7	**2**	0.1	0.01	99[b]

a, 20 min; *b*, 100 min

Further and more compelling evidence came from crossover experiments involving the α-(alkoxy)allylstannanes **6** and **7** prepared as shown in eq. 2.[2]



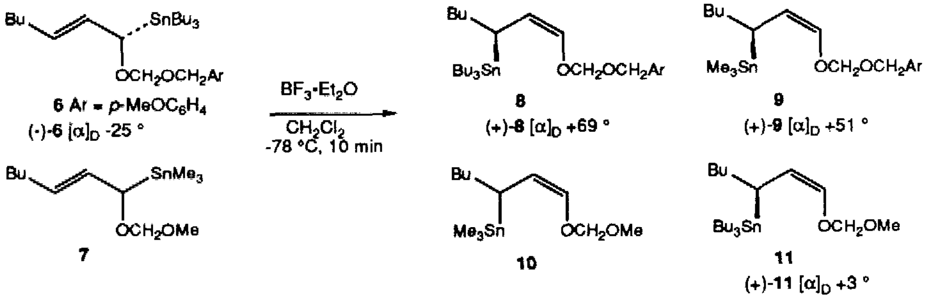
5

6 R = Bu, R' = p-$MeOC_6H_4CH_2$
7 R = Me, R' = Me

(2)

(a) R_3SnLi, THF; (b) p-$MeOC_6H_4CH_2OCH_2Cl$; (c) $MeOCH_2Cl$

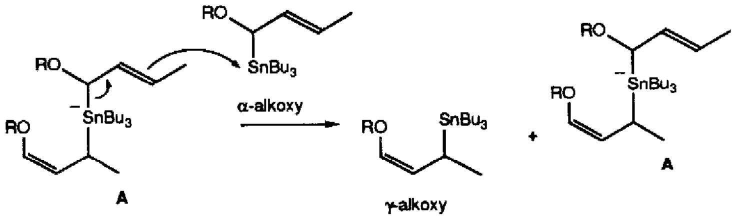
A 1:1 mixture of α-(alkoxy)allylstannanes **6** and **7** was converted within 10 min at -78° C in the presence of BF_3•OEt_2 to a nearly equal mixture of **8**, **9**, **10** and **11** (eq. 3). Ratios were determined from the vinylic γ-proton signals which were clearly resolved in the ^1H NMR spectrum of the mixture. The individual γ-(alkoxy)allylstannanes could also be isolated by preparative TLC on silica gel.



(3)

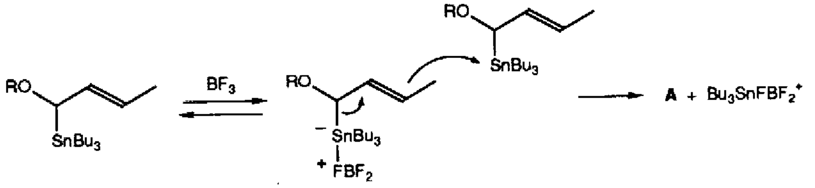
In contrast to the above result, a 1:1 mixture of the γ-(alkoxy)allylstannanes **8** and **10** was recovered unchanged with $BF_3 \cdot OEt_2$ at -78° C. The 1,3-isomerization thus appears to be irreversible in these systems.

Interestingly, when we repeated the crossover experiment using an equimolar mixture of nonracemic (-)-**6** and racemic **7** the product (+)-**11**, derived from Bu_3Sn transfer to racemic **7**, showed small but definite optical rotation. *This finding implies that the Bu_3Sn stannylating agent is chiral.* A possible pathway consistent with these results can be formulated with the novel pentacoordinated stannane **A** serving as a catalytic transfer intermediate (eq. 4).[11]



(4)

Intermediate **A** could arise through BF_3 assisted destannylation of the α-(alkoxy)allylstannane (eq. 5). Because of its catalytic role, only trace amounts of **A** would be required.



(5)

In principle either of the two allyl-Sn bonds of **A** could cleave. However, the failure of γ-(alkoxy)-allylstannanes **8** and **10** to equilibrate indicates that the depicted one is the more labile. Of the several catalysts examined to date only $BF_3 \cdot OEt_2$ has proven effective in the α-(alkoxy)allyl system. No reaction was observed upon treatment of stannane **1** with CF_3CO_2H, Bu_4NF or Me_3SnCl at -78° C. Anhydrous HCl gave only protonolysis whereas $TiCl_4$ and Et_2AlCl caused decomposition.

It should be noted that the process depicted in eq. 4 should be applicable to other allylstannane exchanges, as well. Studies on applications of these findings are in progress.

Acknowledgement: Support from the National Institutes of Health (MCHA 5R01 GM29475) and the National Science Foundation (CHE-8615569) through Research Grants is gratefully acknowledged. We thank Prof. John Dawson and Ms. Alma Bracete for assistance with CD studies.

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4. The absolute configuration of the α-(hydroxy)allylstannane precursors of II and IV was deduced from ^{1}H NMR shifts of the vinylic H signals of the O-methyl mandelates, as previously described, following the method of Trost, *et al.*[2,6,7] Additional evidence supporting these assignments has now been obtained from the CD spectrum of the *p*-bromobenzoates according to the method of Nakanishi and Sharpless.[8] We have also effected a direct chemical correlation of stannane **1** with (*S*)-2-octanol.[6] All three methods give consistent results.

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10. The δ and J values are as follows: **8**; 6.02 ppm 6.2 Hz: **9**; 6.06 ppm, 6.2 Hz: **10**; 5.96 ppm, 6.2 Hz: **11**; 5.93 ppm, 6.3 Hz.

11. An ee of 36% was calculated for the sample of (-)-**6** employed in this experiment. An authentic sample of (-)-**11** prepared by 1,3-isomerization of (+)-**2** of 50% ee showed a rotation of -69° (c 1.36, CH_2Cl_2). Thus the asymmetric transfer leading to (+)-**11** is 3°/0.36 + 69°/0.50=6%.

12. For experimental evidence in support of such stannate complexes, see Reich, H. J.; Phillips, N. H. *J. Am. Chem. Soc.* **1986**, *108*, 2102.

(Received in USA 27 September 1989)