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On the Synthesis of Aryl Cyclopropanes from γ-Benzenesulfonylalkyl Tin derivatives and n-Butyllithium.

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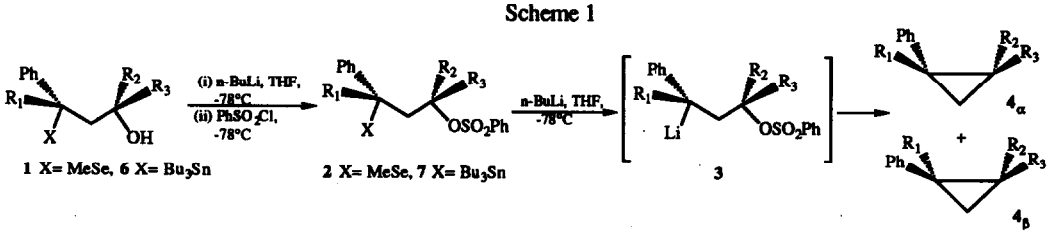
γ-Benzenesulfonyloxyalkyl tin derivatives readily available from γ-hydroxyalkyl selenides, n-butyllithium and trialkyl tin chlorides react with n-butyllithium and stereospecifically lead to aryl cyclopropanes. The transformation is quite general and allows the synthesis of α,β-di- and trisubstituted ones.

We recently disclosed [1] that γ-hydroxyalkyl selenides **1** bearing a seleno group on the benzylic carbon are transformed with reasonably high stereospecificity to aryl cyclopropanes **4** on sequential reaction with benzenesulfonyl chloride and n-butyllithium and that the stereochemical course of this transformation is compatible either with (i) retention or (ii) inversion at each of the two reactive sites (Scheme 1, entries 2 and 4).

We now report new results concerning the transformation of related γ-hydroxyalkyl tin derivatives **6** to aryl cyclopropanes **4** which proved to be completely stereospecific (Scheme 1). Although several efficient routes to γ-hydroxyalkyl tin derivatives exist [2c-e,g] or could be envisaged, we decided to use as the starting material the stereochemically pure γ-hydroxyalkyl selenides **1** we have in hand expecting, that the methylseleno / trialkyltin exchange would proceeds stereoselectively. This proved not to be the case as it will be shown below.

Scheme 1



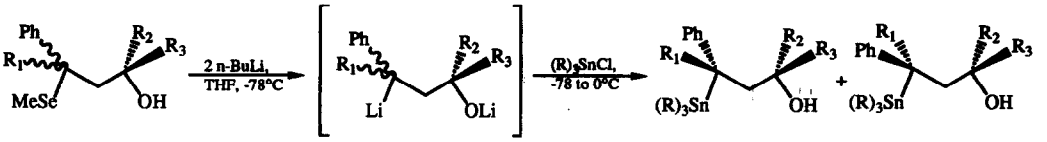
1 X= MeSe, 6 X= Bu_3Sn 2 X= MeSe, 7 X= Bu_3Sn 3

Entry	Starting material	R_1	R_2	R_3	X	Yield in 4 % from 7 ($4_\alpha/4_\beta$)
1	$\mathbf{6a}_\alpha$	H	Ph	H	$(n\text{-}Bu)_3Sn$	69 (100/0)
2	$\mathbf{1a}_\alpha$	H	Ph	H	MeSe	64 (81/19)[1]
3	$\mathbf{6a}_\beta$	H	H	Ph	$(n\text{-}Bu)_3Sn$	67 (100/0)
4	$\mathbf{1a}_\beta$	H	H	Ph	MeSe	74 (97/03)[1]
5	$\mathbf{6b}_\alpha$	Me	H	Me	$(n\text{-}Bu)_3Sn$	56 (100/0)

The synthesis of **6** was readily achieved from γ-hydroxyalkyl selenides **1** and n-BuLi through a sequence of reactions which involves the C-Se bond cleavage on the intermediary lithium γ-alkoxyalkyl selenides and reaction of the resulting functionalized benzyllithiums **5** with trimethyl- or tri(n-butyl)

chlorostannane [(a) 2 equiv. n-BuLi, THF, -78°C, 1h (b) R_3SnCl (R= Me, Bu), THF, -78 to +20°C, 1h] (Scheme 2).

Scheme 2



1 5 6_α 6_β

Entry	R_1	R_2	R_3	R	Yield in **6** % ($6_\alpha/6_\beta$) from **1**
1	H	Ph	H	n-Bu	81 (70/30)
2	H	Ph	H	Me	62 (40/60)
3	Me	H	Me	n-Bu	47 (83/17)
4	Me	H	Me	Me	60 (60/40)

Unfortunately however, this transformation led to a mixture of both stereoisomers of **6a** and **6b** whether a stereoisomeric mixture of **1a** ($\mathbf{1a_\alpha/1a_\beta}$: 48/52) or **1b** ($\mathbf{1b_\alpha/1b_\beta}$: 34/66) or stereoisomerically pure $\mathbf{1a_\alpha}$, $\mathbf{1a_\beta}$, $\mathbf{1b_\alpha}$ or $\mathbf{1b_\beta}$ was used. These ratio are close to 6/4 when chlorotrimethylstannane was reacted and more divergent with its n-butyl analogue. This implies that lithium γ-alkoxyalkyl benzyllithiums **5** are stereochemically unstable under these conditions and loose integrity of their configuration. The interactions between the groups present on **5** and the incoming electrophile dictate therefore the stereoisomeric outcome of this reaction and led to results dramatically different from the ones we have reported above for the reaction of the benzenesulfonates **2** derived from γ-hydroxyalkyl selenides **1** with butyllithiums.

The synthesis of the cyclopropane derivatives **4** was achieved by sulfonation of **6** [(i) n-BuLi, THF-hexane, -78°C (ii) $PhSO_2Cl$, 20°C, 1h, quantitative yield in **7**] and further reaction of the solution of γ-benzenesulfonyloxyalkyl trialkyltin derivatives **7** with n-butyllithium [n-BuLi, THF, -78°C, 0.7h, Scheme 1, entries 1, 3, 5]. This reaction when performed on pure stereoisomers [3] of **6a** and **6b** proved to be completely stereospecific and by far more selective than the one involving related γ-hydroxyalkyl selenides **1** especially when the cis stereoisomer was expected (Table 1 compare entry 1 to 2 and entry 3 to 4).

We have determined unambiguously the stereochemistry of the cyclopropane derivatives [1] but have been unable to do so for the γ-hydroxyalkyl trialkyltin derivatives or for their benzenesulfonates. We nevertheless suggest, based on the behaviour of the same derivatives towards Lewis acids [2] and of related reaction on γ-benzenesulfonyloxyalkyl selenides,[1] that the stereochemical outcome of the cyclisation reaction is as depicted in Scheme 2. The reaction reported here complements the one involving γ-hydroxyalkyl tin derivatives and Lewis acids [2] since it favourably applies to those derivatives bearing the hydroxyl group on a primary or secondary carbon whereas the later exclusively applies to those bearing this group on a tertiary carbon atom.[2]

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References and notes.

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3. This purification performed on column chromatography proved to be more efficiently achieved than that of their seleno analogues.

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