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Synthesis of Selenolates from Stannyl and Silyl Alkylselenides

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Abstract: Stannyl and silyl alkylselenides have been efficiently transformed to the corresponding alkylselenolates on reaction with butyllithiums. Other conditions proved to be limited.

In the course of our studies on C-Se bond cleavage in cyclic selenoacetals derived from of 4-t-butyl cyclohexanone, we needed to transform, for structural determination purposes, related tributylstannyl and tris (trimethylsilyl)silyl selenides to their methylseleno analogues.[1] Although few reports [2] deal with such type of transformation, we encountered some difficulties which led us to study in more details the cleavage of Se-Sn and Se-Si bond. We report here our preliminary study in that field. The stannyl methylselenides **3** required have been first prepared by an extension of the method described [3] in the literature using methylselenol and trialkylstannyl halides in the presence of triethylamine (Scheme 1).

Scheme 1

$$\underset{\mathbf{1}}{R_3SnCl} + \underset{\mathbf{2}}{MeSeH} \xrightarrow[20°C,\ 2h]{Et_3N,\ ether} \underset{\mathbf{3}}{R_3Sn\text{-}SeMe}$$

Entry	R	N°	Yield in 3%
1	Me	**3a**	78
2	nBu	**3b**	80

The yields are high but the method requires the synthesis of bad smelling and easily oxidised selenols. We carried out a more straightforward procedure involving the introduction of similar reagents in a different order.[4] This method takes advantage of the efficient synthesis of lithium trimethylstannylselenolate **5** on reaction of trimethylstannyl lithium with elemental selenium and its alkylation with n-decylbromide (Scheme 2).

Scheme 2

$$\underset{\mathbf{4}}{Me_3Sn\text{-}SnMe_3} \xrightarrow[\text{(ii) Se, 20°C, 0.5h}]{\text{(i) nBuLi, THF, -25°C, 0.5h}} \underset{\mathbf{5}}{\left[Me_3SnSeLi\right]} \xrightarrow[20°C,\ 1h]{n\text{-}C_{10}H_{21}Br,} \underset{\mathbf{6}\quad 65\%}{Me_3Sn\text{-}Se(CH_2)_9\text{-}Me}$$

We next turned our attention to the cleavage of tin-selenium bond in the above mentioned products. We first observed that methyl trimethylstannylselenide **3a** easily reacts with equivalent amount of methyl iodide to give dimethylselenide **7a** in quantitative yield and iodotrimethylstannane. The reaction is however much slower with its tributylstannyl homologue **3b** from which dimethylselenide **7a** is obtained, under similar conditions, in very poor yield. In such case, alkylation of dimethylselenide leading to trimethylselenonium iodide, efficiently competes with the former process. Moreover under similar or forced conditions (THF, reflux or DMF, 100°C) both stannylselenides **3** proved to be inert towards several organic halides such as ethyl-, pentyl iodides and benzyl chloride.

We finally found very efficient conditions to cleave the Sn-Se bond in order to generate the corresponding selenolates. Indeed both stannylselenides **3** easily reacted with n-butyllithium at -78°C to afford lithium methylselenolate **8** whose alkylation with n-decylbromide or benzyl bromide led to methyl n-decylselenide or methyl benzylselenide in very good yields (Scheme 3).

Scheme 3

$$\underset{\mathbf{3}}{R_3Sn\text{-}SeMe} \xrightarrow[\text{-}[R_3SnBu]]{\text{nBuLi, THF, -78°C, 0.5h}} \underset{\mathbf{8}}{\left[LiSeMe\right]} \xrightarrow[\text{then } 20°C]{R'X,\ \text{-}78°C} \underset{\mathbf{7}}{R'\text{-}Se\text{-}Me}$$

Entry	R	R'X	N°	Yield in **7**%
1	Me	$nC_{10}H_{21}Br$	**7b**	80
2	nBu	$nC_{10}H_{21}Br$	**7b**	83
3	Me	$PhCH_2Cl$	**7c**	78
4	nBu	$PhCH_2Cl$	**7c**	79

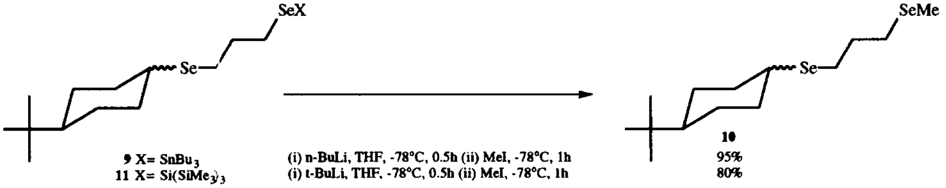
Alternatively, the same transformation can be carried out on reaction of a one to one mixture of methyl trimethylstannylselenide **3a** and n-decylbromide in the presence of an excess of caesium fluoride and catalytic amount of 18-crown-6 as described in Scheme 4. These conditions were recently described for the synthesis of symmetric dialkyl selenides from bis(triphenystannyl)selenide.[5]

Scheme 4

$$\underset{\mathbf{3a}}{Me_3Sn\text{-}SeMe} + C_{10}H_{21}Br \xrightarrow[\text{MeCN, 20°C, 8h}]{\text{2 eq. CsF, 0.2 eq. 18-Crown-6}} \underset{\mathbf{7b}}{Me(CH_2)_9\text{-}SeMe}$$

Applying the first procedure to the butylstannylselenide **9** obtained by reduction of a cyclic selenoacetal derived from 4-t-butyl-cyclohexanone, we obtained, in a nearly quantitative yield, the corresponding methylselenide **10** which was needed for structure determination.[1]

Scheme 5



Transformation of the related tris(trimethylsilyl)selenide **11** was more difficult and even the two conditions which proved successful for the tin derivative were not applicable. Performing however the reaction with t-butyllithium instead of n-butyllithium afforded again the methylselenide **10** in high yield.

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