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THE REACTIONS OF LITHIOBISPHENYLSELENOMETHANE WITH CHLOROMETHYLTRIMETHYLSILANE AND IODOMETHYLTRIMETHYLSTANNANE : NOVEL 1,1 - AND 1,2- ELIMINATION REACTIONS IN ORGANOSELENIUM/ ORGANOTIN CHEMISTRY

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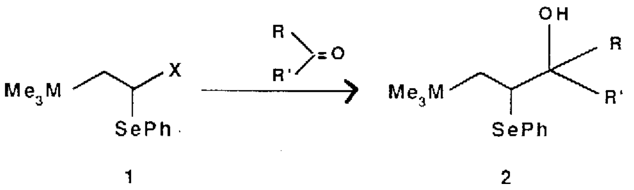
Summary : Anomalous and unprecedented 1,1- and 1,2-elimination reactions are reported in the alkylation of lithiobisphenylselenomethane **4** with chloromethyltrimethylsilane and iodomethyltrimethylstannane.

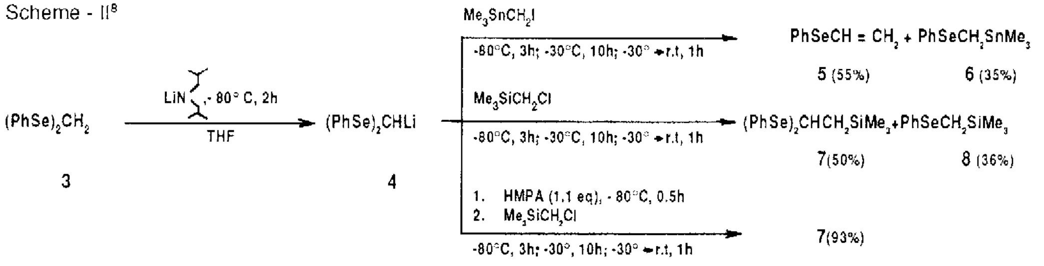
As part of our work[1] on the development of new and efficient routes to $\sigma-$ allylmetallics of silicon[2] and tin,[3] we have explored the possibility of a direct synthesis of $\beta-$ hydroxyselenides **2** from interaction of aldehydes and ketones with $\alpha-$lithiomethyl selenides **1** (M = Si / Sn; X = Li) (Scheme I), the latter being available from bisphenylselenoacetals **1** (M = Si / Sn; X = SePh) by Se/Li exchange[4] with n-BuLi. In this letter we wish to report the successful preparation of **1** (M = Si; X= Li), its reactions with carbonyl compounds and the unprecedented 1,1- and 1,2 - elimination reactions which precluded the synthesis of its tin analog.

Scheme - I



Previous studies of Seebach[5] indicated the possibility of obtention of the necessary bisphenylselenoacetals **1** (M = Si / Sn ; X= SePh)in high yields by alkylation of lithiobisphenylselenomethane **4** with appropriate organometallic halides. Surprisingly , when **4**, prepared from bisphenylselenomethane **3** and lithium diisobutylamide under the conditions described by Seebach, [5] was treated with iodomethyltrimethylstannane [6] (Scheme II) , none of the desired monoalkylated product **1** (M= Sn ; X = SePh) could be traced in the crude reaction product by ^{1}H-NMR . Instead, the major products form this reaction were identified as the vinylselenide **5** and phenylselenomethyltrimethylstannane **6** formed in about 55% and 35% yields, respectively. On the other hand reaction of **4** with chloromethyltrimethylsilane gave the desired monoalkylated product **7** (50%) accompanied by about 36% of phenylselenomethyltrimethylsilane **8**, the latter product could be practically eliminated when the alkylation was carried out in presence of HMPA [7]. Incidentally, the product composition from **4** and iodomethyltrimethylstannane remained unaltered even in the presence of HMPA under conditions which gave only **7**.

Scheme - II[8]



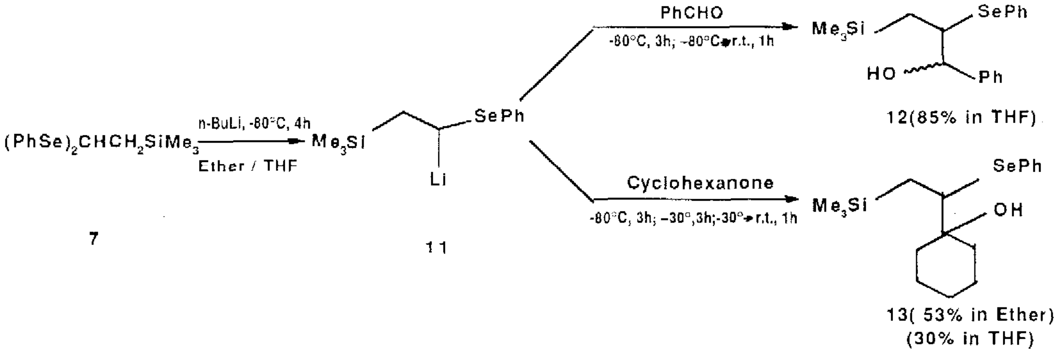
The isolation of **6** and **8** clearly points to the previously undetected dissociation of **4**(1,1- elimination) to form an equilibrium[9] mixture: $4 \rightleftharpoons 9 + 10$[14] (Scheme III). Perhaps the somewhat reduced reactivity of chloromethyltrimethylisilane as compared to the usual alkylating agents[10] results in the unusual product **8**, but then the case with the tin reagent[11] remains somewhat difficult to explain. The formation of phenylvinylslenide **5** is rationalized by the hitherto unknown spontaneous deselenostannylation (1,2-elimination [12]) of the initially formed monoalkylated product **1** (M=Sn; X = SePh).

Scheme - III

$$\underset{\mathbf{4}}{(PhSe)_2\,CHLi} \rightleftharpoons \underset{\mathbf{9}}{PhSeLi} + \underset{\mathbf{10}}{:CHSePh}$$

The monoalkylated product **7** was found to undergo Se/Li exchange with n-BuLi without event[13] (Scheme IV) to give the α - lithioselenide **1 1**. Preliminary studies on **1 1** indicated it to have the virtues of at least moderate necleophilicity. For example, **1 1** gave the β-hydroxyselenides **1 2**[1](1 : 1 mixture of diastereomers) and **1 3** in good yields.

Scheme - IV[8]



The synthetic utility of **1 1** as well as of the novel deselenostannylation (1,2 - elimination) reaction is currently under active investigation in this laboratory.

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References and Notes :

(1) T. K. Sarkar and S. K. Ghosh, *Tetrahedron lett.*, **1 9 8 7**, *28*, 2061; (2) For recent reviews, see : P. Magnus, T. Sarkar and S. Djuric, " Comprehensive Organometallic Chemistry" G. Wilkinson, Ed. Pergamon Press - New York, Vol 7, **1 9 8 2**; W.P. Weber, "Silicon Reagents for Organic Synthesis", Springer-Verlag, Berlin, 1983; E. Colvin, "Silicon in Organic Synthesis, Butterworths, London, **1 9 8 1**; (3) For a recent review, see : M. Pereyre, J-P. Quintard and A. Rahm, "Tin in Organic Synthesis", Butterworths, London, **1 9 8 7**; (4) For a recent review, see : C. Paulmier, "Selenium Reagents and Intermediates in Organic Synthesis", Pergamon Press, New York, **1 9 8 6**; (5) D. Seebach and N. Peleties, *Chem.Ber.*,**1 9 7 2**, *105*,511; C. Raucher and G. A. Koolpe, *J. Org. Chem.*, **1 9 7 8**, *43*,3794; (6) D. Seyferth and S. B. Andrews, *J. Organometallic Chem.*, **1 9 7 1**, *30*.151; (7) M. Sevrin and A. Krief, *Tetrahedron Lett.*, **1 9 8 0**, 585; (8) Yields refer to material purified by chromatography on silica gel. All compounds reported were homogeneous by TLC analysis and showed ^{1}H-NMR, IR and mass spectra consistent with the assigned structures. The identity of **5**, **6** and **8** were further confirmed by comparison with independently synthesized samples; (9) For 1, 1- elimination in related sulfur series, see : D. Seebach, *Chem. Ber.*,**1 9 7 2**, *105*, 487. See also, ref. 5.; (10) Like Raucher (ref. 5) we also found that alkylating agents, such as MeI or Me_3SiCl give clean monoalkylation products with 4 uncontaminated with any side products ; (11) Pearlman reported the much higher reactivity of iodomethyltrimethylstannane as compared to its silicon analog; B. A. Pearlman, S. R. Putt, and J. A. Fleming, *J. Org. Chem.*, **1 9 8 5**, *50*,3622; (12) For 1, 2-elimination in the related sulfur series, see : M. Ochiai, S. Tada, K. Sumi and E. Fujita, *Tetrahedron Lett.*, **1 9 8 2**, *23*, 2205; (13) The overriding influence of the phenylseleno group (–SePh) on the formation and stability of **1 1** is noteworthy, since the trimethylsilyl group is known to disfavour carbanions β to it : W. Engel, I. Fleming and R. H. Smithers, *J. Chem. Soc. Perk I*, **1 9 8 6**, 1637; (14) The fate of this species has not been investigated.

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