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**Preliminary communication**

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# SYNTHESIS OF α-SILYLSELENOALKYLLITHIUMS

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## Summary

The α-silylselenoacetals $(RSe)_2CR'SiMe_3$ react with n-BuLi in THF at —78°C to give the lithium derivatives $RSeCR'(SiMe_3)Li$; reaction of the latter with alkyl halides and carbonyl species have been examined.

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The high reactivity of α-silylselenides [1] indicates that they have considerable synthetic potential, and the availability of general routes for their synthesis is thus desirable. Contradictory reports have appeared recently concerning the synthesis of trimethylsilylselenophenylmethyllithium from the corresponding trimethylsilylselenophenylmethane [1a,b].

We have found that trimethylsilylselenophenylmethane (Ia) is deprotonated by lithium diisopropylamide (LDA) in THF (—30°C/0.5 h) to give the corresponding lithium derivative II in 80% yield. Further treatment with n-decyl bromide gives 1-trimethylsilyl-1-phenylselenoundecane (75% yield) and treatment with heptanal gives 1-trimethylsilyl-1-phenylseleno-2-octanol (17% yield) and the corresponding 1-phenylseleno-1-octene (13%). The temperature (—30°C) is crucial: less than 5% metalation is observed at —78°C for 3 h, and if heptanal is added at this temperature it is quantitatively deprotonated. However, this metalation is not general. Neither the higher homolog 1-trimethylsilyl-1-phenylselenoundecane nor the closely related trimethylsilylmethylselenomethane are metalated under the same or modified reaction conditions.

We have found a more general route to α-silylselenoalkyllithiums which takes advantage of the easy cleavage of a carbon—selenium bond. Thus, α-silylselenoacetals (Ib) react readily with n-BuLi in THF at —78°C to give quantitatively the desired organometallics II. This reaction is very efficient and seems not to be limited by the nature of the substituent directly attached to the carbanionic center or to the selenium atom. Furthermore, alkylation of II gives III in high yield, whereas reaction with aldehydes or ketones produces the β-hydroxy-α-silylselenides IV in moderate yield, along with some vinylselenide V arising from $Me_3SiOH$ elimination in IV (Scheme 1, Table 1).

SCHEME 1

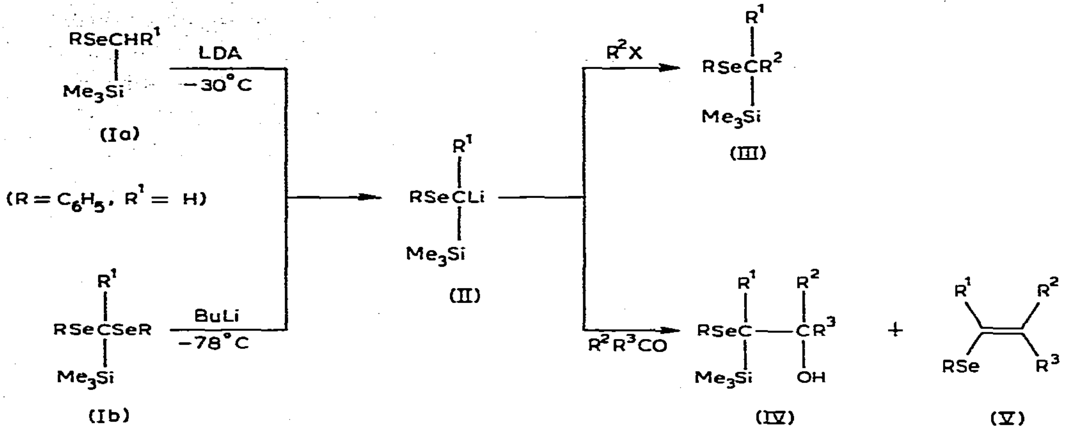


TABLE 1

REACTIONS OF ALKYL BROMIDES AND CARBONYL COMPOUNDS WITH α-SILYLSELENOALKYLLITHIUMS (R = $CH_3$)

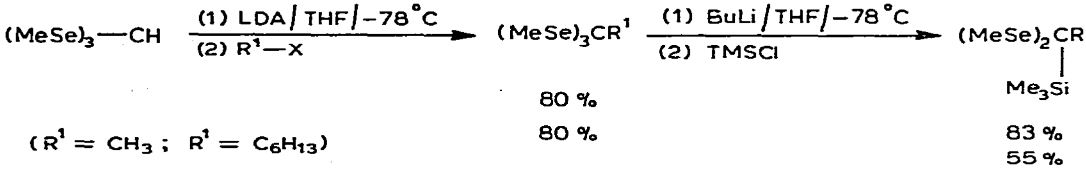
| $R^1$ | $R^2$ | Yield of III (%) [a] | $R^1$ | $R^2$ | $R^3$ | Yield of IV (%) [a] |
|---|---|---|---|---|---|---|
| $CH_3$ | $C_6H_{13}$ | 80 | $CH_3$ | H | $C_6H_{13}$ | 40 |
| $CH_3$ | $C_{10}H_{21}$ | 95 | $CH_3$ | H | $C_{10}H_{21}$ | 50 |
| $C_6H_{13}$ | $C_4H_9$ | 80 | $CH_3$ | $(CH_2)_5$ | | 40 |
| | | | $CH_3$ | $CH_3$ | $C_9H_{19}$ | 35 |

[a] The spectral data (IR, NMR and mass spectra) are fully in accord with the proposed structures.

The formation of IV is remarkable in view of the ease with which α-silyl alcoholates bearing a carboxylate or a phosphorus or sulfur derivatives α to the silyl group decompose into the corresponding olefin, as a result of $Me_3SiO$ elimination [3].

Hitherto unknown α-silylselenoacetals Ib used in this procedure were synthesized in good yield from methylseleno *ortho*-esters [4] according to Scheme 2.

SCHEME 2



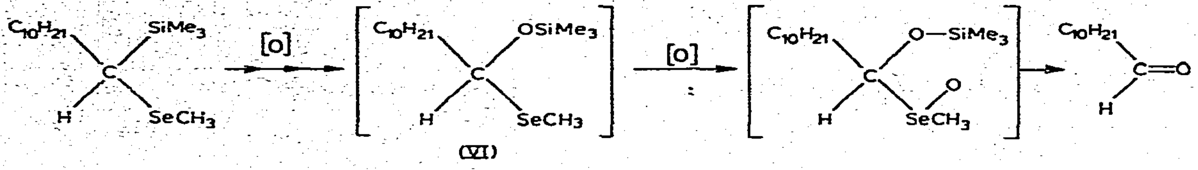
$$(MeSe)_3\text{—}CH \xrightarrow[(2)\ R^1\text{—}X]{(1)\ LDA/THF/-78^\circ C} (MeSe)_3CR^1 \xrightarrow[(2)\ TMSCl]{(1)\ BuLi/THF/-78^\circ C} (MeSe)_2\underset{\displaystyle Me_3Si}{\underset{|}{C}}R^1$$

$(R^1 = CH_3;\ R^1 = C_6H_{13})$ 80 %, 80 %; 83 %, 55 %

Reactions of some of the new species have been examined, e.g. either $H_2O_2$ (30% in $H_2O$) in THF or $NaIO_4$ reacts with 1-trimethylsilyl-1-methylselenoundecane to give undecanal in 77% yield, and the former reagent transforms the 1,1-bis(methylseleno)trimethylsilylheptane into heptanoic acid in 82% yield. In the first case, the aldehyde formation can be explained by the oxidative rearrangement depicted in Scheme 3, and this is supported by the independent transformation [6] of the postulated intermediate, O-silylhemiselenoacetal (VI) [5] to the corresponding undecanal.

Further studies of the β-hydroxy-α-silyl compounds are under investigation.

SCHEME 3



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