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1,1-BIS(PHENYLSELENO)- AND 1,1-BIS(METHYLSELENO)-ALKYLLITHIUMS AS BUILDING BLOCKS IN ORGANIC SYNTHESIS *

D VAN ENDE A CRAVADOR and A KRIEF

Department of Chemistry, Facultés Universitaires N D de la Paix, 61 rue de Bruxelles, B 5000 Namur (Belgium)

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Summary

1,1-Bis(phenylseleno)alkyllithiums are conveniently prepared from the corresponding selenoacetals and lithium tetramethylpiperidide in HMPT/THF 1,1-Bis(methylseleno)alkyllithiums, not available by similar procedures are quantitatively obtained from 1,1,1-tris(methylseleno)alkanes and n-BuLi. These carbanions are treated with a large variety of electrophiles and the resulting products further transformed.

Introduction

Whereas the n-BuLi-promoted cleavage of the C—Se bond in methylseleno- and phenylseleno-acetals and -ketals is a well established reaction [1] which occurs rapidly and quantitatively in THF (−78°C, <0.2 h; $>95\%$ yield), little was known [1a,2] about the metallation of selenoacetals. A recent report [3] in this field prompted us to publish the results below

Results and discussion

As expected the ease of metallation dramatically decreases from bis(phenylseleno)-methane (Ia) or -ethane (Ib) to bis(phenylseleno)heptane (Ic) or higher homologues, 1,1-bis(methylseleno)alkanes being the most difficult to deprotonate (Scheme 1). For example Ia is easily metallated with lithium diisobutylamide [1a] or diisopropylamide (LDA) in THF, while Ib requires the presence of HMPT (LDA, THF/HMPT; −30°C, 0.2 h, method A) for its successful deprotonation and higher homologues give disappointing results under similar conditions. However use of lithium tetramethylpiperidide (LTMP) [4] (in

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* Dedicated to Professeur H Normant on the occasion of his 72nd birthday on June 25th 1979.

TABLE 1

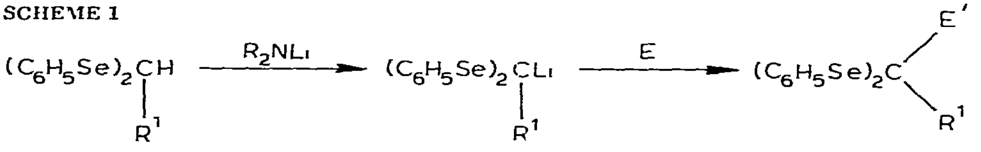
REACTIONS OF ELECTROPHILES WITH 1,1-BIS(PHENYLSELENO)ALKYLLITHIUMS

R^1	E	E′	Method used [a]	Yield of III (%) [b]
CH_3	$C_{10}H_{21}Br$	$C_{10}H_{21}$	A	74
CH_3	$C_{10}H_{21}Br$	$C_{10}H_{21}$	B	83
C_6H_{13}	$C_6H_{13}Br$	C_6H_{13}	A	44
C_6H_{13}	$C_6H_{13}Br$	C_6H_{13}	B	86
C_6H_{13}	ethylene oxide	CH_2CH_2OH	B	88
C_6H_{13}	$C_6H_5CH{=}O$	$HOCHC_6H_5$	B	75

[a] The electrophile was added to the lithium reagent during 0.2 h at −30°C, then allowed to reach 0°C and stirred at this temperature for 1 h before the usual work up. [b] The spectral data (IR, NMR, mass spectrometry) fully agree with the proposed structures.

THF/HMPT, −30°C, 0.2 h, method B) in place of LDA leads to a high percentage of metallation (>80%) in the cases studied (Scheme 1, Table 1).

SCHEME 1



(I) (II) (III)

(Ia, IIa, R^1 = H,
Ib, IIb, R^1 = CH_3,
Ic, IIc, R^1 = C_6H_{13})

Analoguous bis(methylseleno)alkanes were not metallated under similar conditions. Use of stronger bases such as alkyllithiums in more polar solvents than THF or a higher temperature do not solve the problem, and exclusive C—Se bond cleavage was observed [1d]. Interestingly the closely related bis(phenylseleno) analogues are partially metallated under these conditions. For example, treating n-BuLi in THF with bis(phenylseleno)alkanes Ia—Ic as already described (Scheme 1) but at higher temperatures (−50°C or +25°C instead of −78°C) leads to an increased percentage of metallation (−78°C no metallation; −50°C; IIa, 35%; IIb, 15%, IIc, 0%; +25°C; IIa, 55%, IIb, 25%, IIc, 0%) at the expense of carbon—selenium bond cleavage and similar behaviour is observed when more polar solvents are used (DME, −78°C, IIa, 50%; IIb, 35%; IIc, 22%; THF/HMPT: 9/1, −78°C; IIb, 26%).

1-Lithio-1,1-bis(methylseleno)alkanes (II′) which cannot be made directly, can be quantitatively prepared from tris(methylseleno)alkanes (IV′) and n-BuLi via selenium—metal exchange [1], which instantaneously occurs in ether or THF at −78°C (Scheme 2). Under the usual conditions the reactions are performed at −78°C in THF for 0.5 h prior addition of electrophiles. Examples are given in Tables 2a and 2b and Scheme 2.

Particularly interesting is the exclusive C—Se bond cleavage observed with

TABLE 2a

ALKYLATION OR HYDROXYALKYLATION OF 1 1-BIS(METHYLSELENO)ALKYLLITHIUMS(II') (SCHEME 2)

R^1	E	E'	Yield of V' (%) [a]
H	$(CH_3)_3SiCl$	$(CH_3)_3Si$	72
CH_3	$(CH_3)_3SiCl$	$(CH_3)_3Si$	83
C_6H_{13}	$C_6H_{13}Br$	C_6H_{13}	75
C_6H_{13}	C_4H_9Br	C_4H_9	80
CH_3	propylene oxide	$CH_2CHOHCH_3$	83

[a] The spectral data (IR NMR and mass spectra) fully agree with the proposed structure

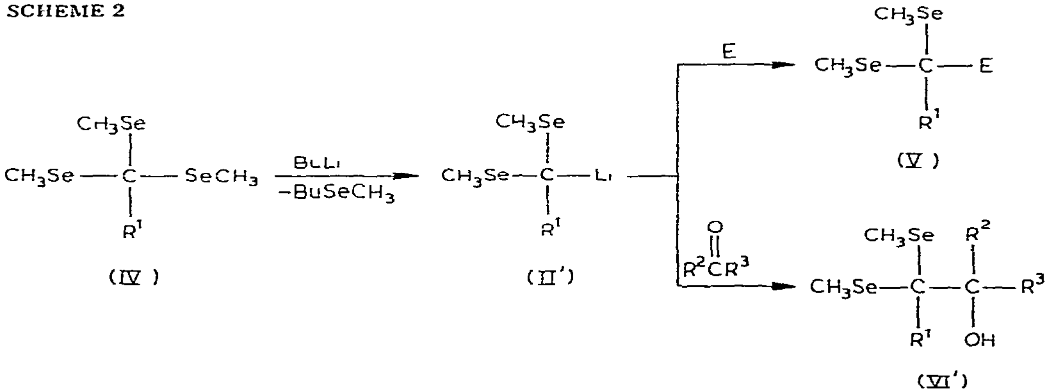
TABLE 2b

REACTION OF 1 1-BIS(METHYLSELENO)ALKYLLITHIUMS (II') WITH CARBONYL COMPOUNDS (SCHEME 2)

R^1	R^2	R^3	Yield of VI' (%) [a]
CH_3	H	C_6H_{13}	65
CH_3	H	$C_{10}H_{21}$	56
CH_3	CH_3	C_9H_{19}	45
C_6H_{13}	H	C_6H_{13}	70
C_6H_{13}	H	$C_{10}H_{21}$	72
C_6H_{13}	CH_3	C_9H_{19}	40

[a] The spectral data (IR NMR and mass spectra) fully agree with the proposed structures

SCHEME 2



the parent compound tris(methylseleno)methane (Table 2a, entry 1) (addition of the *ortho*-ester to the THF solution of n-BuLi is required), for which metallation is also possible [1a]. The latter reaction was easily and quantitatively performed by LDA in THF at —78° C, and the resulting carbanion was trapped by several electrophiles (Scheme 3 and Table 3).

SCHEME 3

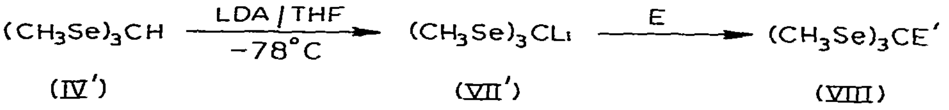


TABLE 3

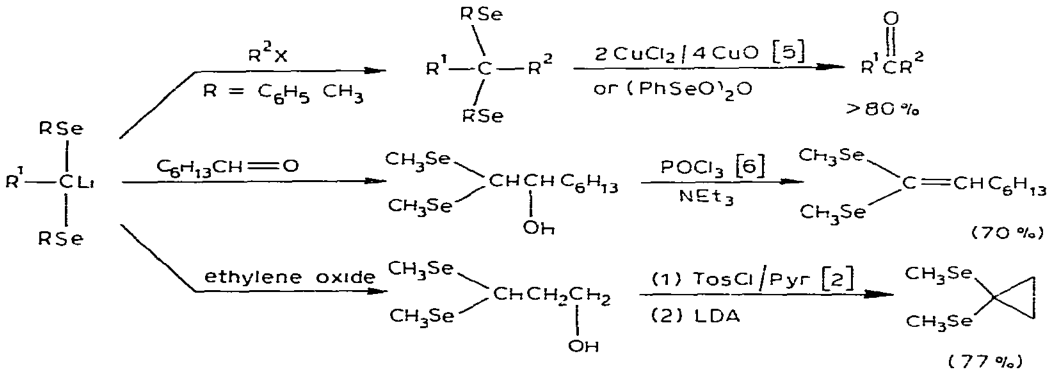
REACTION OF TRIS(METHYLSELENO)METHYLLITHIUMS WITH ELECTROPHILES (SCHEME 3)

E	E′	Yield of VIII (%) [a]
$C_6H_{13}Br$	C_6H_{13}	80
$C_{10}H_{21}Br$	$C_{10}H_{21}$	66
CH_3I	CH_3	80
propylene oxide	$CH_2HOCHCH_3$	70
$C_6H_{13}CH{=}O$	$HOCHC_6H_{13}$	75

[a] Spectral data (IR NMR and mass spectra) fully agree with the proposed structures

The transformations presented in Scheme 4 clearly demonstrate the synthetic value of the reagents described.

SCHEME 4



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