

SELENIUM STABILIZED CARBENIUM IONS
BIS(SELENO)- AND BIS(THIO)-ALKYLATION OF KETONES AND ALDEHYDES

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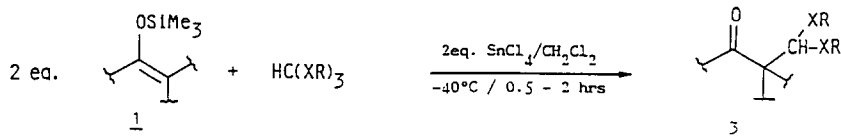
The title reactions have been carried out in high yield by reacting Lewis acid activated thio- and seleno-orthoformates with silyl enol ethers derived from aldehydes and ketones.

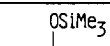
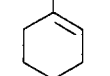
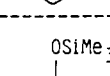
In recent work we have shown that stable bis(seleno)-carbenium ions could be generated from tris(methylseleno)-orthoesters and triphenylcarbenium ion ¹ or by protonation of ketene selenoacetals ². We have also observed that the species generated in the former way reacted sluggishly with 1-trimethylsilyloxycyclohexene to give the corresponding bis(seleno)-alkylated ketone in low yield ³. The excellent results we obtained for the Lewis acid mediated seleno-alkylation of ketones ⁴ prompted us to reinvestigate the title reactions under modified conditions. We wish to report herein on the formation of carbenium ionic species stabilized by two sulfur or two selenium atoms which proved to be excellent alkylating agents (Scheme) ⁵.

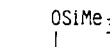
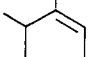
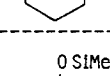
It can be seen that all these reactions take place rapidly to give thio- or selenoacetals of β -keto-aldehydes 3 in excellent yield when two equivalents of silyl enol ether 1 and two equivalents of SnCl₄ are used. Stoichiometric mixtures of 1 and 2 lead to lower yield (72-77 %) in 3; in these cases some of the starting orthoester 2 is recovered (~20 %). No significant difference can be detected in reactivity of cyclic (5 or 6 membered) or open chain silyl ethers; there is however a slight difference between methyl- and phenylseleno-orthoesters, the latter giving nearly quantitative yields in almost every cases. Furthermore, entries 4, 5 and 6 show that the reactions proceed with complete regioselectivity.

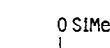
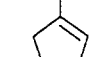
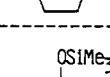
Formation of products 3 can be viewed as equivalent to selective thio- and/or seleno-acetalisation of β -ketoaldehydes or 1,3-dialdehydes. Possible further transformations of these interesting compounds are currently under investigation.

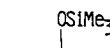
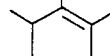
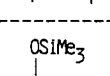
Scheme

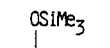
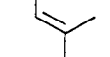
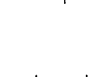


Entry	<u>1</u>	XR in <u>2</u>	Product <u>3</u> , yield (%) ⁵
1		SeMe	<u>3a</u> , 98 (77) [§]
2		SePh	<u>3b</u> , 95
3		SMe	<u>3c</u> , 91

4		SeMe	<u>3d</u> , 72
5		SePh	<u>3e</u> , 97
6		SMe	<u>3f</u> , 87

7		SeMe	<u>3g</u> , 77
8		SePh	<u>3h</u> , 88
9		SMe	<u>3i</u> , 95

10		SeMe	<u>3j</u> , 92
11		SePh	<u>3k</u> , 94
12		SMe	<u>3l</u> , 86

13		SeMe	<u>3m</u> , 83
14		SePh	<u>3n</u> , 92
15		SMe	<u>3o</u> , 70

(§) Reaction carried out using 1 equivalent of 1 (10 % of 2 recovered)

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References and Notes

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2. H. Wautier, S. Desauvage and L. Hevesi, *J. Chem. Soc. Chem. Commun.*, 738 (1981).
3. B. Georges, Mémoire de Licence, University of Namur, 1982.
4. K.M. Nsunda and L. Hevesi, *Tetrahedron Letters*, **25**, 4441 (1984).
5. Elemental analysis and spectroscopic (IR, ¹H NMR, Mass) data are in agreement with the proposed structures of products 3.

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