Tetrahedron Letters,Vol.30,No.33,pp 4433-4434,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

REACTIONS OF SELENIUM STABILIZED ALLYLIC CARBOCATIONS WITH 1-(TRIMETHYLSILYLOXY)CYCLOHEXENE.

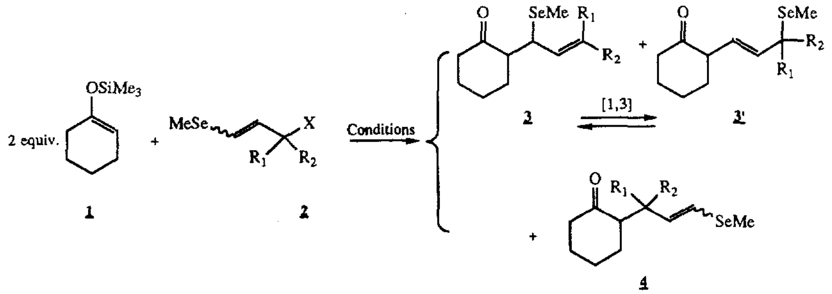
L. HEVESI * and A. LAVOIX

Department of Chemistry, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles
B-5000 NAMUR - Belgium

***Summary** : In favorable cases the title reactions occur efficently and with high regioselectivity; they allow interesting functionalization of a simple carbonyl compound through allylic selenoxide syn-elimination and/or [3,2] sigmatropic rearrangement.*

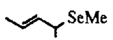
During the past few years, we have studied various physical and chemical properties of selenium stabilized carbenium ions [1]. Investigation of the reactivity of these species demonstrated the efficiency of a number of C-C bond forming reactions [2] which may be useful in organic synthesis. Herein we wish to report our preliminary results about the reactions of the title species with silyl enol ethers, specific examples of which are shown in Scheme 1.

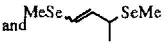
Scheme 1



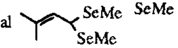
Entry	2	R_1	R_2	X	Conditions	Yield % 3 (3 : 3')	Yield % 4
1	2a (E)	H	H	SeMe	2 equiv. $SnCl_4$ / CH_2Cl_2 / -40°C / 6h	-	27 [a]
2	2b [b]	H	Me	SeMe	2 equiv. $SnCl_4$ / CH_2Cl_2 / -40°C / 6h	32 (0 : 100)	18
3	2c [c]	Me	Me	SeMe	2 equiv. $SnCl_4$ / CH_2Cl_2 / -40°C / 2h	69 (80 : 20)	-
4	2d (E)	H	H	OH	1.2 equiv. $ZnCl_2$ / CH_3NO_2 / R.T. / 0.5h	-	15
5	2e (Z)	H	Me	OH	1.2 equiv. $ZnCl_2$ / CH_3NO_2 / R.T. / 3h	44 (0 : 100)	9
6	2f (Z)	Me	Me	OH	1.2 equiv. $ZnCl_2$ / CH_3NO_2 / 0°C / 1h 1.2 equiv. $ZnCl_2$ / CH_3NO_2 / -40°C / 1.5h	80 (80 : 20) 69 (96 : 04)	- -

a) 51% of 2a (E + Z) recovered unreacted

b) 2b is a [1,3] sigmatropic mixture of 

and 

(ref. 4)

c) 2c is in fact the pure acetal 

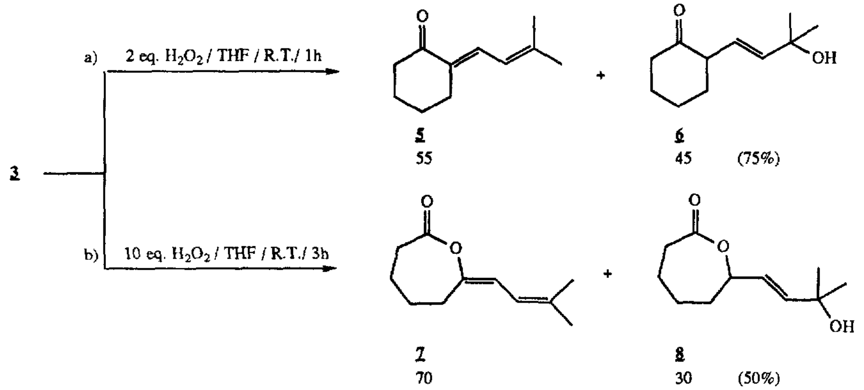
The electrophilic species [3] can be generated from 1,3-bis(methylseleno)propenes [4] 2a-c using 2 equiv. of tin tetrachloride as Lewis acid, in dichloromethane solution, as well as from 3-hydroxy vinyl selenides [4] 2d-f in the presence of zinc chloride in nitromethane. In both cases the reactivity of selenium substituted electrophiles, the efficiency and the regiochemistry of the reactions strongly depend on the number of alkyl groups (R_1, R_2 = Me) present in the allylic position of precursors 2. Thus, the parent 1,3-bis(methylseleno)propene 2a reacts slowly to give a low yield of 4 (R_1, R_2 = H) exclusively. Increase of the reaction time for 2d does not improve the yield. Introduction of a methyl group in allylic position of 2 increases its reactivity and improves the yields substantially (Scheme 1, entries 2,5), but gives a mixture of 3 (in fact 3') and 4 (R_1 = H, R_2 = Me). Surprisingly, the [1,3] sigmatropic equilibrium [4,5] between 3 and 3' is found completely displaced on the side of 3' in these cases. Finally, when two methyl groups are present in the cation precursor (Scheme 1, entries 3,6), the reactions lead exclusively and in good yield to a mixture of 3 and 3' (R_1 = R_2 = Me). Apparently in these cases 3 is favoured not only by the substitution pattern, but also by lower reaction temperatures (entry 6).

The above results closely resemble those obtained when precursors 2a-f have been reacted with N-methylpyrrole [2c]

Since, on reaction with 1-(trimethylsilyloxy)cyclohexene 2f gave a good yield of almost pure 3 ($R_1 = R_2 = Me$), we have also examined shortly the oxidative deselenylation reactions of the latter compound.

Selenides such as 3 are easily oxidized to the corresponding selenoxides by a series of common oxidizing agents [6], and the fate of the selenoxides so produced depends largely on their structural environment. Allylic selenoxides such as the one derived from 3 can undergo either the well known syn elimination reaction or a [3,2] sigmatropic rearrangement leading to an allylic selenenate which hydrolyses instantaneously to the corresponding allyl alcohol. Usually the latter reaction largely predominates over the former so that the allyl alcohol arising from the rearrangement-hydrolysis sequence is the sole isolated product [7]. However, treatment of 3 with 2 equivalents of hydrogen peroxide in THF led to both the elimination and the rearrangement products 5 and 6, respectively, in a close to 1 : 1 ratio (Scheme 2, a). Lowering the reaction temperature down to -50°C did not change this ratio significantly.

Scheme 2



On the other hand, carrying out the oxidation of 3 using a large excess (10 eq.) of hydrogen peroxide changes completely the outcome of the reaction, since now the mixture of lactones 7 and 8 are isolated in a 7 : 3 ratio (Scheme 2b). The moderate 50 % yield may be caused by side reactions due to the use of excess oxidant. Undoubtedly, compounds 7 and 8 arise from one sort of coupling between selenoxide syn elimination (or [2,3] sigmatropic rearrangement) and Baeyer-Villiger oxidation [8] of ketone 5 (or 6). Indeed, in separate experiments we could transform 5 to 7 (or 6 to 8) in excellent yield by treating 5 (or 6) with $MeSeO_2H$ / 3 eq. H_2O_2 / THF / R.T) [9]

Since compounds 5 and 6 on one hand, 7 and 8 on the other hand are easily separated by chromatography on silica gel, the selectivity displayed in Scheme 2 allows to prepare them in a straightforward manner from simply available precursors [10]. Work is being done to establish the generality and to further increase the selectivity of the above transformations.

References and notes

1. a) Hevesi, L. ; Piquard, J.L. ; Wauthier, H. ; J. Am. Chem. Soc, **1981**, *103*, 870 ; b) Wauthier, H. ; Desauvage, S. ; Hevesi, L. ; J. Chem. Soc., Chem. Commun., **1981**, 738 ; c) Hevesi, L. ; Desauvage, S. ; George, B. ; Evrard, G. ; Blanpain, P. ; Michel, A. ; Harkema, S. ; van Hummel, G.J. ; J. Am. Chem. Soc., **1984**, *106*, 3784 ; d) Ösapay, K. ; Delhalle, J. ; Nsunda, K.M. ; Rolli, E. ; Houriet, R. ; Hevesi, L. ; J. Am. Chem. Soc., **1989**, in press.
2. a) Halazy, S. ; Hevesi, L. ; J. Org. Chem. **1983**, *48*, 5242 ; b) Renard, M. ; Hevesi, L. ; Tetrahedron Lett., **1983**, *24*, 3911 ; c) Renard, M. ; Hevesi, L. ; J. Chem. Soc., Chem. Commun., **1986**, 688 ; d) Hevesi, L. ; Renard, M. ; Proess, G. ; ibid., **1986**, 1725 ; e) Hevesi, L. ; Nsunda, K.M. ; Tetrahedron Lett., **1984**, *25*, 4441 ; f) ibid., **1985**, *26*, 6513 ; g) idem, J. Chem. Soc., Chem. Commun., **1987**, 1519.
3. These appear indeed as selenium stabilized allylic carbocation equivalents, but they are most likely present in solution as Lewis acid-precursor complexes and not as free carbocations : Dieden, R. ; Hevesi, L. ; Unpublished results.
4. For preapartion of these precursors, see : Renard, M. ; Hevesi, L. ; Tetrahedron, **1985**, *41*, 5939.
5. a) Sharpless, K.B. ; Lauer, R.F. ; J. Org. Chem., **1972**, *37*, 3973 ; b) Di Giamberardino, T. ; Halazy, S. ; Dumont, W. ; Krief, A. ; Tetrahedron Lett., **1983**, *24*, 3413.
6. Reich, H.J. in "Oxidation in Organic Chemistry", Part C, Ed. W.S. Trahanovsky, Academic Press, New York, 1978, Chapter 1.
7. For a review, see : Reich, H.J. in "Organoselenium Chemistry", Ed. D. Liotta, Wiley Interscience, New York, 1987, Chapter 8.
8. For another example of such a coupling but in a more simple case, see our ref. 2e.
9. Seleninic acids have been described to give, on reaction with hydrogen peroxide, "peroxyseleninic" acids able to perform the Baeyer-Villiger reaction : a) Grieco, P.A. ; Yokoyama, Y. ; Gilman, S. ; Ohfune, Y. ; J. Chem. Soc., Chem. Commun., **1977**, 870 ; b) Williams, J.R. ; Lever, J.D. ; Synthesis, **1977**, 427.
10. All new compounds described in this paper displayed spectral (IR, 1H NMR, MS) data and in some cases elemental analyses in full agreement with the proposed structures.

(Received in UK 3 July 1989)