Tetrahedron Letters,Vol.28,No.42,pp 4925-4928,1987   0040-4039/87 $3.00 + .00
Printed in Great Britain   Pergamon Journals Ltd.

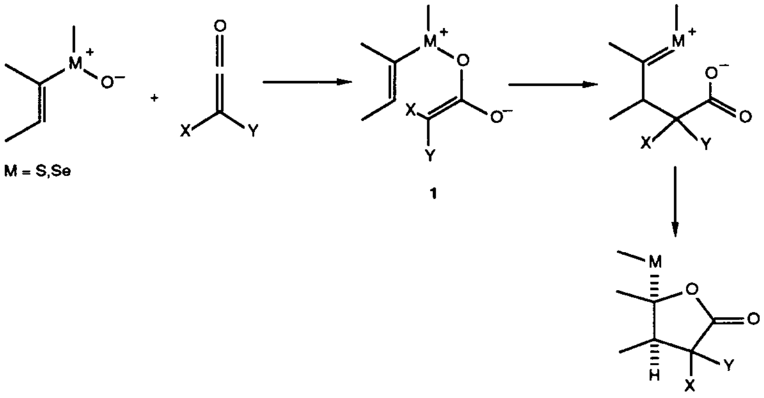
REACTIONS OF VINYL SELENOXIDES AND KETENES
VIA 3,3-SIGMATROPIC REARRANGEMENT

J. P. Marino* and Min Woo Kim
Department of Chemistry, The University of Michigan,
Ann Arbor, Michigan 48109

Summary: The reactions of several vinyl selenoxides with chlorocyanoketene proceed *via* a 3,3-sigmatropic rearrangement of an enolate oxyselenonium species to yield seleno-substituted γ-butyrolactones.

Our recent discovery[1] of a new 3,3-sigmatropic rearrangement of oxysulfonium intermediates **1** generated from vinyl sulfoxides and haloketenes prompted us to explore the generality of this process using vinyl selenoxides. Furthermore, our previous reports centered on the use of haloketenes generated from the zinc-promoted dechlorinations of α-chloro acid chlorides. In an effort to extend this methodology to other ketenes which did not involve the use of zinc/zinc chloride, we examined the chemistry of chlorocyanoketene and vinyl selenoxides. A generalized version of the reaction process is shown in Scheme I.

Scheme I



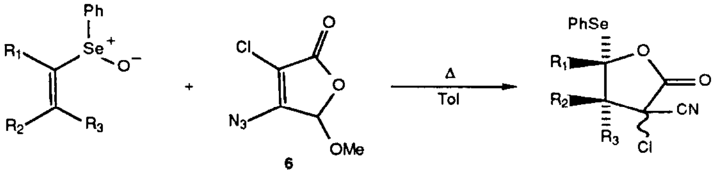
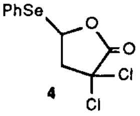
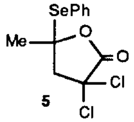
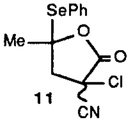
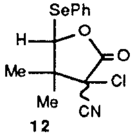
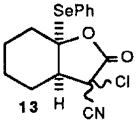
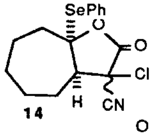
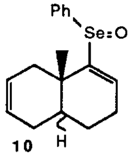
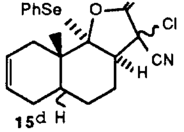


TABLE I

Selenoxide	Ketene	Lactone	Yield
$R_1=R_2=R_3=H$ **2**	DCK	 **4**	50%
$R_1=Me$ $R_2=R_3=H$ **3**	DCK	 **5**	55%
3	CCK	 **11**	30%[b]
$R_1=H$ $R_2=R_3=Me$ **7**	CCK	 **12**	30%
$R_1,R_2=(CH_2)_4$ $R_3=H$ **8**	CCK	 **13**	75%[c]
$R_1,R_2=(CH_2)_5$ $R_3=H$ **9**	CCK	 **14**	75%
 **10**	CCK	 **15**[d]	30%

[a] DCK ≡ Dichloroketene generated from 15-20 eq. of trichloroacetyl chloride and zinc/copper couple.
CCK ≡ Chlorocyanoketene generated from **6**.

[b] Chlorocyanolactone was unstable to chromatography. Yield is given for dechlorinated lactone.

[c] Yield is for crude chlorocyanolactone which was unstable to purification. The yield of purified dechlorinated lactone was 50%

[d] This product is a mixture of four diastereomers, three of which could be isolated pure.

The replacement of selenium by sulfur in the above reaction presents both advantages and disadvantages. On the one hand, the selenoxide bond is much more polarized than the analogous sulfoxide group[2] rendering the oxygen of selenoxides more nucleophilic and hence more reactive. At the same time, selenoxides are more easily deoxygenated by metals such as zinc and are more difficult to access in an optically pure state.

We initially subjected two simple vinyl selenoxides,[3] namely phenyl vinyl selenoxide **2** and phenyl isopropenyl selenoxide **3**, to the dichloroketene reaction using zinc/copper couple to generate the ketene. In both cases, a good yield (50-60%) of the expected phenyl selenenyl γ-butyrolactones **4** and **5** was realized. This success was soon dampened when cyclohexenyl phenyl selenoxide was treated with zinc and trichloroacetyl chloride. In this case, only reduction of the selenoxide to the selenide was observed. In fact, attempts to employ the zinc method of ketene generation on any β-substituted vinyl selenoxide only resulted in reduction. Apparently, the more substituted vinyl selenoxides reacted more slowly with the ketene than the zinc/copper couple.

For the above reasons, we examined the reactivity of vinyl selenoxides with chlorocyanoketene,[4] which is conveniently generated by thermolysis of 4-azido-3-chloro-5-methoxy-2(5H)-furanone **6**. The aforementioned heterocycle is easily prepared in two steps and readily cleaves to chlorocyanoketene and methyl formate in refluxing benzene or toluene. We prepared a series of acyclic and cyclic vinyl phenyl selenoxides[5] (**3**, **7-10**) and reacted them with 1.2 eq. of furanone **6** in refluxing toluene over a period of 2 hours. Removal of the solvent and column chromatography (silica gel) of the reaction mixtures yielded the diastereomeric butyrolactones (**11-15**) in a ratio of ∿1.5 to 1. It was not possible to definitively assign[6] the structures of the diastereomers by ^{1}H-NMR. In some cases (**11** and **13**), the chlorocyanolactones were unstable to chromatography, and the chlorine was removed immediately by aluminum amalgam reduction.[7] The results of the lactonization reactions are summarized in Table I.

Our experience with the reactions of vinyl selenoxides contributes to the generalization of the 3,3-sigmatropic rearrangement depicted in Scheme I. In addition, the use of chlorocyanoketene reveals that zinc chloride or a zinc enolate is not a requirement for the success of the rearrangement.

Acknowledgments: We are pleased to acknowledge the support of NIH (CA 22237-08) for this research.

References

1. (a) Marino, J. P.; Fernandez, R. Tetrahedron Lett. **1985**, 25, 5381.
   (b) Marino, J. P.; Perez, A. D. J. Am. Chem. Soc. **1984**, 106, 7643.
   (c) Marino, J. P.; Neisser, M. O. J. Am. Chem. Soc. **1981**, 103, 7687.
2. Agenas, L.-B. Chapter 5 in Organic Selenium Compounds, Klayman, D. L.; Gunther, W. H., Eds., John Wiley and Sons, New York, N.Y., **1973**.
3. These selenoxides were prepared by the oxidation of the corresponding selenides with 1.2 eq. of mCPBA in methylene chloride at -78°C. The selenides were obtained from the reaction of the appropriate vinyl Grignard and diphenyl diselenide.
4. Fishbein, P. L.; Moore, H. W. J. Org. Chem. **1984**, 49, 2190.
5. Selenoxides were prepared as in reference 3. The selenides **7-10** were prepared from the appropriate ketones via their selenoketals. The selenoketals were treated with 1.2 eq. of methyl iodide in DMF from R.T. to 85°C. After extraction of the reaction mixture with water, the vinyl selenides were isolated by column chromatography on silica gel.
6. Diastereomeric ratios were determined from integration of signals of key protons in lactone rings. Chemical shifts for specific protons in lactone products are: **11**, CH_3, 1.89 and 2.09 (1.2:1); **12** H_γ, 5.79 and 5.77 (2:1); **13**, H_β, 2.69 and 2.90 (2:1); **14**, H_β, 3.36 and 3.07 (1.2:1); **15**, H_β, 3.33-3.73 (2:2.8:1), mixture of four diastereomers.
7. See Ehrenstein, M.; Johnson, A. R. J. Org. Chem. **1946**, 11, 823 for preparation of aluminum amalgam. Reductions were carried out with 20 eq. of Al in a solvent mixture of THF/H_2O/MeOH (10/1/1) at room temperature for 2 hours. Reaction mixtures were extracted with ether, and products were isolated by column chromatography (silica gel).

(Received in USA 7 May 1987)