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HIGHLY SELECTIVE anti-MARKOWNIKOFF TYPE OXIDATION OF OLEFINIC BONDS OF ALLYLIC ALCOHOL DERIVATIVES. SPECIFIC SYNTHESIS OF β-ALKOXY α-PHENYLSELENO CARBONYL COMPOUNDS

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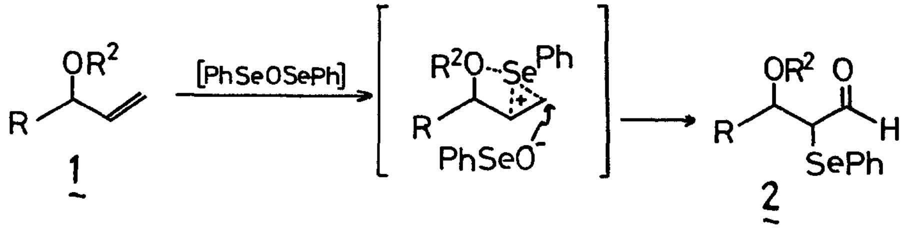
Summary: On treatment with diphenyl diselenide and benzeneseleninic anhydride, 3-t-butyldimethylsiloxy-1-alkenes were converted to the corresponding α-phenylseleno aldehydes exclusively.

The one-step transformation of olefins to α-functionalized carbonyl compounds[1] has enabled the use of easily accessible olefinic compounds as convenient sources for preparing versatile synthetic intermediates. While regioselective oxidation of terminal olefins to functionalized methyl ketones has been accomplished by several methods,[2] difficulties are usually encountered for their oxidation in anti-Markownikoff manner, e.g., direct conversion of terminal olefins to the corresponding aldehydes.[3]

Recently, we have briefly shown that allyl benzyl ethers undergo regioselective introduction of carbonyl functionality into the sp^2 carbon remote from the alkoxy group.[1d] More detailed studies on the oxidation of allyl alcohol derivatives with diphenyl diselenide and t-butyl hydroperoxide, or diphenyl diselenide and benzeneseleninic anhydride[4] led to an efficient one-step preparation of α-phenylseleno aldehydes from the corresponding 3-t-butyldimethylsiloxy-1-alkenes.

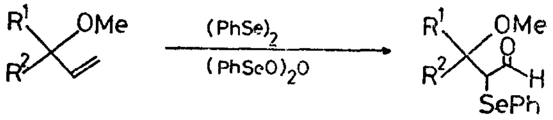


On examining various 3-hydroxy-1-alkene derivatives, we assumed that the steric and electronic effects for their ether analogues would be important factors which direct the site of introducing carbonyl functionality. Indeed, anti-Markownokoff type oxidation is found to proceed with allylic ethers in highly regioselective manner as described below.

Among a variety of allylic ethers, trialkylsilyl ethers appear to be the most promising due to their steric bulkiness, electron inductive ability, and the easy availability through silylation.[5] Allyl trimethylsilyl ethers were too labile to hydrolysis and did not survive the present oxidation conditions,[6] but t-butyldimethylsilyl analogues 1[7] showed enough stability and an excellent preference for regioselectivity. Thus, treatment of 3-*t*-butyldimethylsiloxy-1-alkene 1 with a mixture of diphenyl diselenide and benzeneseleninic anhydride resulted in the formation of 3-*t*-butyldimethylsiloxy-2-phenylseleno aldehyde 2 exclusively.[8]

The following procedure is representative.[9] To a toluene (5 ml) solution of diphenyl diselenide (874 mg, 2.8 mmol) and benzeneseleninic anhydride (504 mg, 1.4 mmol) was added a toluene (15 ml) solution of 3-*t*-butyldimethylsiloxy-1-decene (540 mg, 2.0 mmol). After stirring for 30 min under refluxing, the reaction mixture was washed with satd aq NaCl and the aqueous layer was extracted with ether. Removal of the solvent followed by purification by silica gel column chromatography afforded 3-*t*-butyldimethylsiloxy-2-phenylselenodecanal[10] (764 mg, 87%) and diphenyl diselenide (1.03 g).

Terminal olefins possessing tertiary substituted carbon at allylic position are known to be attacked by hypohalites in the *anti*-Markownikoff manner.[11] In the present case, allyl methyl ethers 3 were also oxidized to the corresponding α-phenylseleno aldehydes 4 exclusively.[12]

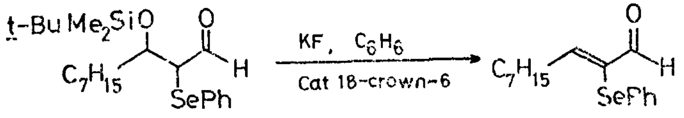


3 4

Further transformation of the above products to α-phenylseleno enals[13] was readily accomplished by employing fluoride anion as a base.[14] Treatment of 5 with KF (5 eq) in the presence of a catalytic amount of 18-crown-6 (0.1 eq) for 12 hr at room temperature gave the corresponding α-phenylseleno enal 6 in good yield. In addition, 3-butyl-3-methoxy-2-phenylselenoheptanal 7 was also converted into the α-phenylseleno enal 8 by heating with silica gel.

Moreover the pronounced effect of *t*-butyldimethylsilyl group is also evident for allylic alcohol derivatives possessing internal double bonds. 4-*t*-Butyldimethylsiloxy-5-phenyl-2-pentene and 3-*t*-butyldimethylsiloxycyclohexene were also found to undergo similar oxidation to afford the corresponding β-siloxy α-phenylseleno ketones exclusively.[15]

Since allylic alcohols are in general readily available via a variety of standard routes and their silylation usually proceeds in high yields,[7] the present work demonstrates a simple and highly versatile approach to α-phenylseleno enals or enones.



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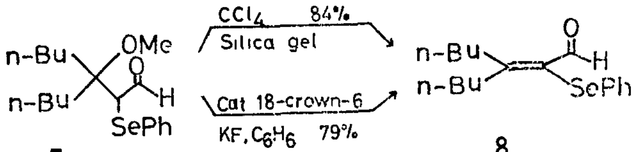
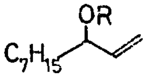
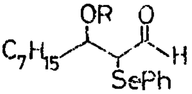
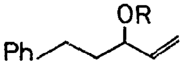
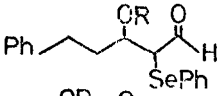
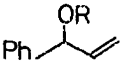
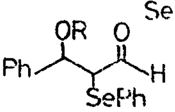
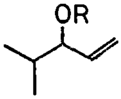
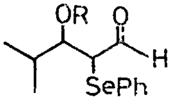
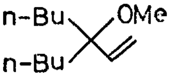
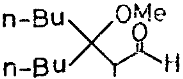
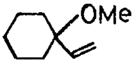
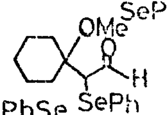
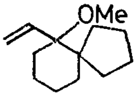
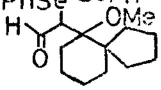
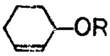
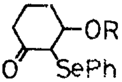
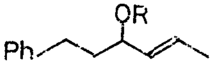
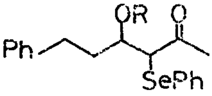


7 8

Table. Oxidation of 1 with $(PhSe)_2$ and $(PhSeO)_2O$.

Allylic Ether 1	Product 2	Yield,%
		87
		81
		79
		74
		93
		89
		trace
		76
		89

R = $\underline{t}$-BuSi(Me)$_2$

References and Notes

(1) (a) K. B. Sharpless and A. Y. Teranishi, *J. Org. Chem.*, **38**, 185 (1973); (b) (b) G. Cardillo and M. Shimizu, *ibid.*, **42**, 4268 (1977); (c) I. Kuwajima and M. Shimizu, *Tetrahedron Lett.*, 1277 (1978); (d) M. Shimizu, R. Takeda, and I. Kuwajima, *ibid.*, 419 (1979).

(2) (a) T. Takahashi, N. Nagashima, and J. Tsuji, *ibid.*, 799 (1978); (b) S. Raucher, *ibid.*, 2261 (1978), and ref 1b-1d.

(3) (a) F. Freeman, P. J. Cameron, and R. H. DuBois, *J. Org. Chem.*, **33**, 3970 (1968); (b) F. Freeman, R. H. DuBois, and T. G. MacLaughlin, *Org. Synth.*, **51**, 4 (1971).

(4) As previously reported, [PhSeOSePh] was tentatively considered as a reactive species in this reaction, ref 1d.

(5) C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Am. Chem. Soc.*, **85**, 2497 (1963); J. F. Kelbe, H. Finkbeiner, and D. M. White, *ibid.*, **88**, 3390 (1966); E. Nakamura, T. Murofushi, M. Shimizu, and I. Kuwajima, *ibid.*, **98**, 2346 (1976), and references cited therein.

(6) Oxidation of 3-trimethylsiloxy-1-alkenes with (PhSe)$_2$ and (PhSeO)$_2$O led to the formation of 1-alken-3-ones and other products. This type of oxidation of alcohols proceeded cleanly under the same conditions; M. Shimizu and I. Kuwajima, *Tetrahedron Lett.*, submitted for publication.

(7) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972), and references cited therein.

(8) Oxidation of 3-benzyloxy-1-decene gave a 9:1 ratio of 3-benzyloxy-2-phenylselenodecanal and 3-benzyloxy-1-phenylseleno-2-decanone.

(9) (PhSe)$_2$ and *t*-BuOOH was also employable for the oxidation, ref 1d.

(10) A mixture of threo and erythro isomers was usually obtained.

(11) For example, A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968); D. R. Dalton, V. P. Dutta, and D. C. Jones, *J. Am. Chem. Soc.*, **90**, 5498 (1968).

(12) Silica gel deactivated with water (20%) was used for purification of the product.

(13) H. J. Reich and S. K. Shah, *J. Am. Chem. Soc.*, **99**, 263 (1977).

(14) Fluoride anion has been proved to be a relatively weak base; I. Kuwajima, T. Murofushi, and E. Nakamura, *Synthesis*, 602 (1976) and ref 7.

(15) The absence of the regioisomer was confirmed by glpc analysis of the deselenylated product.

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