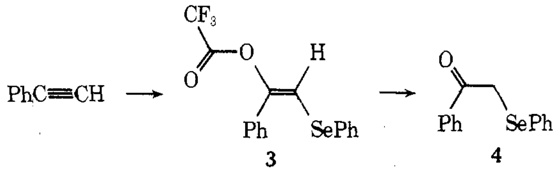
nucleophile in the addition reaction (attack on episeleniranium ion).[9] The conversion of olefins to hydroxy selenides followed by selenoxide elimination[1,2,4] provides a mild and efficient route to allylic alcohols equivalent to the singlet oxygen oxidation of olefins.

Benzeneselenenyl trifluoroacetate also adds rapidly to acetylenes, giving phenylseleno-substituted enol trifluoroacetates. Thus, addition of phenylacetylene to a solution of $PhSeO_2CCF_3$ in benzene gives **3** (stereochemistry as-



sumed): pmr ($\delta_{\text{carbon tetrachloride}}$) 6.63 (s), 7.0–7.5 (m); ir carbonyl frequency at 1799 cm^{-1}; ^{19}F nmr singlet at $\delta_{\text{chloroform-}d}$ ($CFCl_3$) 75.17 ppm. Hydrolysis by shaking with ammonium hydroxide or stirring briefly at room temperature with 1.5 equiv of KOH in ethanol gives the α-phenyl seleno ketone **4** in 68% yield, providing a new route to this type of compound. Under similar conditions, 1-phenylpropyne gives α-phenylselenopropiophenone (67%), previously prepared by reaction of the lithium enolate of propiophenone with PhSeBr.[1] Addition to 3-hexyne gives a single adduct, which upon hydrolysis gives 4-phenylseleno-3-hexacetylene to α-phenyl seleno ketone followed by oxidation and syn elimination[1-3] to give the enone has synthetic po- and synelimination[1-3] to give the enone has synthetic potential, when combined with the variety of methods available for the introduction of acetylenic groups. We are examining the possibility of using the enol trifluoroacetates as precursors for lithium enolates of α-phenyl seleno ketones, since these are not easily accessible by deprotonation.

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References and Notes

(1) H. J. Reich, I. L. Reich, and J. M. Renga, *J. Amer. Chem. Soc.*, **95**, 5813 (1973).
(2) (a) K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **95**, 2697 (1973); (b) K. B. Sharpless, R. F. Lauer and A. Y. Teranishi, *ibid.*, **95**, 6137 (1973).
(3) (a) D. J. L. Clive [*Chem. Commun.*, 695 (1973)] has recently reported the addition of benzeneselenenyl bromide to cyclic enol acetates in the presence of silver trifluoroacetate. $PhSeO_2CCF_3$ may be an intermediate. (b) A. Haas and D. Y. Oh [*Chem. Ber.*, **102**, 77 (1969)] have prepared several sulfenyl trifluoroacetates.
(4) D. N. Jones, D. Mundy, and R. D. Whitehouse, *Chem. Commun.*, 86 (1970).
(5) (a) W. Jenny, *Helv. Chim. Acta.* **41**, 317 (1958); (b) G. Hölzle and W. Jenny, *ibid.*, **41**, 331 (1958); (c) D. D. Lawson and N. Kharash, *J. Org. Chem.*, **24**, 857 (1959).
(6) G. Hölzle and W. Jenny, *Helv. Chim. Acta.* **41**, 593 (1958).
(7) Both PhSeCl (orange) and PhSeBr (purple) are stable, nonhygroscopic crystalline solids which are prepared by cleavage of diphenyl diselenide with sulfuryl chloride and bromine, respectively.
(8) D. E. Janssen and C. V. Wilson, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1973, p 547.
(9) The mechanism of $PhSeO_2CCF_3$ additions to olefins and acetylenes is probably closely related to the extensively studied additions of sulfenyl halides[10] which also show high stereoselectivity, but low regioselectivity in many cases.
(10) E. Kühle, *Synthesis*, 563 (1971).
(11) The trifluoroacetates, particularly where the carbonium ion derived from them is stabilized, are somewhat labile and should be hydrolyzed promptly after the addition.

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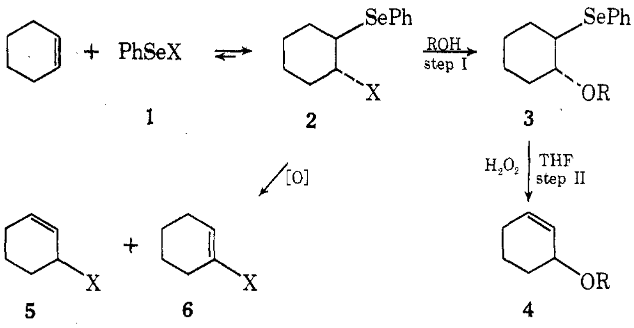
Electrophilic Organoselenium Reagents. A New Route to Allylic Acetates and Ethers

Summary: Phenylselenenyl bromide and acetate undergo electrophilic trans-1,2 addition to olefins. The PhSeBr adducts solvolyze readily in acetic acid or alcohols and oxidation of the resulting products affords allylic acetates and ethers in high overall yield.

Sir: We[1] and others[2] have recently demonstrated the synthetic utility of the gentle olefin forming syn eliminations of alkyl phenyl selenoxides. These olefin syntheses are limited only by the ways in which one can make carbon–selenium bonds. We now report a new route to substituted alkenes based on electrophilic addition of a variety of PhSeX species to olefins (Scheme I). Phenyl selenenyl chloride[3] (**1**, X = Cl), bromide (**1**, X = Br), and acetate[4] (**1**, X = OAc) all readily undergo trans-1,2 addition to olefins as shown in Scheme I for cyclohexene. The adduct **2** is stable when X = OAc but is thermally and solvolytically unstable when X = Cl or Br. Thus oxygen-substituted adducts such as **3** are easily obtained by either direct addition of PhSeOAc or by solvolysis of the corresponding bromide **2** (X = Br) in acetic acid or in alcohols.

Scheme I



Unlike previous procedures[1] we have found it desirable to isolate[5] the intermediate adducts (**3**), which were oxidized (H_2O_2, THF) in a separate step to the desired unsaturated products. Table I reveals that the overall yields for this two-step procedure are quite good.

Table II shows there is strong preference for elimination in the direction which gives the allylic derivative (**5**, Scheme I) rather than the vinylic derivative (**6**, Scheme I) whenever the heteroatom in the X group of **2** is oxygen. This effect has been noted previously,[1a] interestingly when X = Cl elimination occurs equally in both directions.

The following description of the transformation of (*E*)-4-octene to (*E*)-5-acetoxy-3-octene on a moderate scale demonstrates the convenience of the method.

To a stirred solution of 14.9 g (93 mmol) of bromine in 250 ml of glacial acetic acid was added 29.5 g (94.5 mmol) of diphenyl diselenide. After stirring for 15 min a homogeneous dark red solution was obtained. (*E*)-4-octene (21 g, 186 mmol) was added followed by 36.5 g (373 mmol) of anhydrous potassium acetate. An immediate exothermic reaction occurred[4] and the mixture turned a pale yellow-white. After stirring for 1 hr the suspension was diluted with 400 ml of water and extracted twice with 200-ml portions of ethyl acetate. The combined extracts were washed with water and 10% aqueous sodium carbonate, dried, and concentrated to give 62 g of an orange oil. This oil was dissolved in 400 ml of THF and cooled to 6° in an ice bath and 82 ml (950 mmol) of 30% H_2O_2 was added over a 15-min period. After 20 min the cooling bath was removed and the solution allowed to warm. When the mixture

Table I
Conversion of Olefins to Allylic Acetates and Ethers

Olefin	Step I,[a] solvent, hr	Step II,[b] hr, temp	% Yield of allylic acetate or ether[c]
Cyclohexene	HOAc, 4	0.8, reflux	78
		44, rt[d]	73
(*E*)-4-Octene	HOAc, 1	2.5, rt[d]	91 (85)[e]
(*E*)-Cyclododecene	HOAc, 21	1.5, rt[d]	(85)[e]
Cyclohexene	CH_3OH, 1	2, rt[d]	93

[a] The reactions in HOAc were run on a 5-mmol scale; otherwise they are identical with the large scale reaction described for (*E*)-4-octene. The reactions run in methanol (also 5-mmol scale) differ from the HOAc reactions only in that no base, such as KOMe, corresponding to KOAc is added. The PhSeBr is generated *in situ* by adding Br_2 to a solution of PhSeSePh in the appropriate alcohol prior to adding the olefin. The reactions are stirred at room temperature for the indicated time and worked up as in the HOAc cases. [b] A water bath at ambient temperature provides a sufficient heat sink for these smaller scale oxidations. Note that the six-membered cyclic allylic acetate case was unusually slow to eliminate and had to be refluxed for 50 min. [c] Yields were determined by glc except for those in parentheses which were determined by isolation. [d] Room temperature. [e] The *E* olefin appears to be the major product as there is no detectable ir absorption for a *Z*-disubstituted alkene.

Table II
Direction of Elimination in Step II (Scheme I)

2, X[a]	5:6 in Scheme I
OH	99.8:0.2
OAc	97:3
OCH_3	98:3
Cl	51:49

[a] Pure samples of the indicated 1,2 adducts of **2** were oxidized as usual (H_2O_2, THF) and the ratio of their elimination products were determined by glc. All compounds were identified by comparison with authentic materials.

reached 18°, bubbling occurred and the reaction flask was placed back in the ice bath until the temperature of the solution returned to 6°, at which point the bath was removed again and stirring was continued for 2.5 hr at ambient temperature. Water (800 ml) was added and the mixture was extracted with two 200-ml portions of ethyl acetate. The combined extracts were washed with 10% aqueous sodium carbonate,[6] dried, and concentrated to give 34 g of an orange oil. Distillation afforded 26.7 g (85% yield) of pure (*E*)-5-acetoxy-3-octene as a colorless oil [bp 55-57° (5 mm)]; all spectral and analytical data were consonant with the assigned structure.

The reaction, as it now stands, has some important limitations as evidenced by the following observations. Phenyl selenenylacetate adds to both 2-methyl-2-heptene and 1-dodecene to give equal amounts of the two possible adducts in each case. Addition to Δ^2-cholestene also produces a mixture of the two possible diaxial phenyl selenoacetates. Although we were able in some cases to separate the isomeric adducts and oxidize them separately, we are working on variations in the reaction conditions and the nature of the selenium(II) electrophile in hopes of improving both the stereo- and regioselectivities of additions to unsymmetrical olefins. Some olefins (*e.g.*, cholesterol) fail to react altogether.

Finally, it is worth mentioning a curious alternative method we happened upon for addition of the elements of "PhSeOAc" across an olefinic unit. Refluxing cyclohexene in acetic acid for 3 hr with 1 equiv of phenylseleninic acid ($PhSeO_2H$) gave rise to the adduct **3** (R = Ac) in 90% yield.

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References and Notes

(1) (a) K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **95**, 2697 (1973); (b) K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Lett.*, 1979 (1973); (c) K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Amer. Chem. Soc.*, **95**, 6137 (1973).

(2) (a) H. J. Reich, I. L. Reich, and J. M. Renga, *J. Amer. Chem. Soc.*, **95**, 5813 (1973); (b) D. Seebach, private communication; (c) D. L. J. Clive, *Chem. Commun.*, 695 (1973); (d) P. A. Grieco and M. Miyashita, *J. Org. Chem.*, **39**, 120 (1974).

(3) In a recent publication (ref 1c, footnote 3) we stated that PhSeCl could be prepared for use *in situ* by the reaction of sulfuryl chloride with PhSeSePh in CCl_4. This is not true since such solutions contain SO_2 which interferes with subsequent reactions. If such solutions are concentrated to dryness, the SO_2 is removed and the PhSeCl remaining is suitable for the selenenylation of ketones in EtOAc. However, cleavage of PhSeSePh with a stoichiometric quantity of Cl_2 in CCl_4 is the superior method for preparation of PhSeCl.

(4) One can generate PhSeOAc in HOAc free of PhSeBr by reaction of PhSeBr in HOAc with AgOAc. PhSeOAc so generated readily adds to olefins. However, we have found that addition of the "PhSeOAc" moiety to olefins can be accomplished without expensive silver salts by simply adding anhydrous KOAc to a solution of olefin and PhSeBr in HOAc; KBr precipitates almost immediately. It is not clear whether these additions involve direct addition of PhSeOAc or acetolysis of a first-formed PhSeBr adduct (*e.g.*, **2**, X = Br).

(5) Addition of H_2O_2 directly to the HOAc reaction mixtures results in very poor yields.

(6) This alkaline aqueous extract contains $PhSeO_2^-Na^+$. Neutralization with HOAc followed by reduction with excess $NaHSO_3$ afforded 15 g of pure crystalline PhSeSePh (~50% recovery). This was our first attempt to recover the diselenide reagent from a reaction and there is obviously room for improvement.

(7) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient; Alfred P. Sloan Fellow, 1973-1975.

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