Communications

Organoselenium Chemistry. Benzeneselenenyl Trifluoroacetate Additions to Olefins and Acetylenes

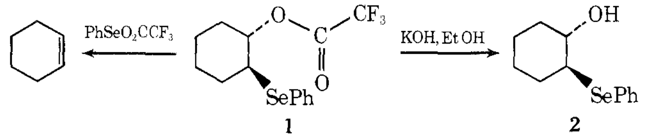
Summary: Benzeneselenenyl trifluoroacetate adds to olefins and acetylenes to give β-trifluoroacetoxyalkyl phenyl selenides and phenylseleno enol trifluoroacetates.

Sir: Recent work has demonstrated the synthetic utility of organoselenium compounds for the effective introduction of unsaturated functions.[1,2] We report here the partial characterization and some reactions of benzeneselenenyl trifluoroacetate.[3] This reagent provides new routes to functionally substituted selenides, and thus to the olefins derived from them by selenoxide elimination.[4]

Only isolated examples of stable selenenic acid derivatives are known;[5] all are aryl derivatives with strong electron-withdrawing substituents. Reactions of these selenenic derivatives with olefins has been studied by Hölzle and Jenny,[6] but the vigorous reaction conditions and difficulty of preparing the required reagents makes their method synthetically unattractive.

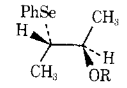
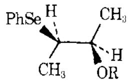
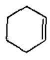
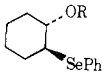
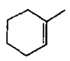
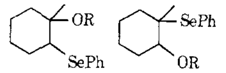
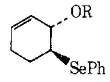
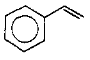
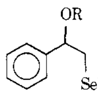
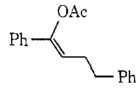
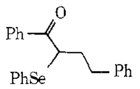
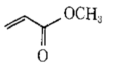
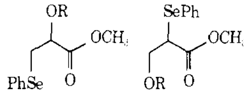
The treatment of benzeneselenenyl chloride or bromide[7] with silver trifluoroacetate[8] in benzene (or other solvents such as ether or methylene chloride) gives a precipitate of silver halide and a yellow or orange solution which has properties consistent with the presence of benzeneselenenyl trifluoroacetate. The ^{19}F nmr spectrum shows a singlet [$\delta_{\text{chloroform-}d}$ (relative to $CFCl_3$) 76.5 ppm],[3b] the proton nmr a multiplet [$\delta_{\text{chloroform-}d}$ (TMS) 7.0–7.5], and the ^{13}C nmr resonances at [δ_{ether} (TMS)] 132.8 (C-1), 134.5 (C-2), 130.2 (C-3), and 130.7 (C-4). The carbon-13 nmr shifts are very close to those observed for PhSeCl (133.2, 134.9, 130.0, 130.8 ppm, respectively) and other selenenyl derivatives that we have examined, such as PhSeBr and PhSeSePh. The ir spectrum (CH_2Cl_2) shows a broad carbonyl absorption at 1727 cm^{-1} (shoulder at 1783 cm^{-1}). This is unexpected, since $CF_3SO_2CCF_3$ shows ir absorptions at 1879 and 1814 cm^{-1}.[3b] It appears that the trifluoroacetate carbonyl must be substantially perturbed by intra- or intermolecular association to reduce the carbonyl frequency. The reagent reacts rapidly with water to give diphenyl diselenide and, presumably, benzeneseleninic acid.

$PhSeO_2CCF_3$ adds quantitatively and virtually instantaneously to olefins, giving β-trifluoroacetoxy selenides. For example, the addition of cyclohexene (1 mmol) to a solution prepared by the addition of PhSeBr (236 mg, 1 mmol) to silver trifluoroacetate (221 mg, 1 mmol) in 5 ml of benzene followed by filtration and evaporation of solvent gave *trans*-2-phenylseleno-1-trifluoroacetoxycyclohexane (1): pmr ($\delta_{\text{carbon tetrachloride}}$) 1.2–2.4 (m, 8 H), 3.20 (td, J = 9, 4 Hz, 1 H), 4.97 (td, J = 8, 4 Hz, 1 H), 7.3 (m, 3 H), 7.55 (m, 2 H); ^{19}F nmr singlet at $\delta_{\text{chloroform-}d}$ ($CFCl_3$) 75.0 ppm; ir carbonyl frequency at 1783 cm^{-1}. Hydrolysis to give 2 (90% yield from cyclohexene) was accomplished by the addition of a benzene solution of 1 to ethanolic potassium hydroxide (25°, 5 min). Other examples are summarized in Table I. The mildness and simplicity of the reaction should allow the presence of many other functionalities.



1
2

Table I
Reaction of Benzeneselenenyl Trifluoroacetate with Olefins

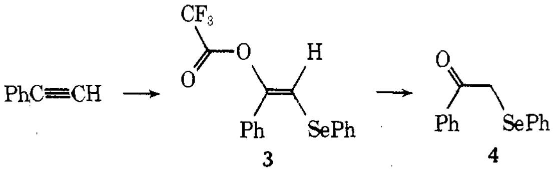
Olefin	Adducts[a] (R = COCF₃)	% yields[b] (R = H)
		92
		94
		90[c]
	 45:55	93
		69
		96[c]
		96
	 35:65	71[c,d]

[a] All compounds were fully characterized by spectroscopic methods. [b] Yields are for material purified by preparative thin layer chromatography. [c] The addition reaction for these olefins was carried out in benzene, others in methylene chloride. [d] Cleavage of the trifluoroacetate was carried out using anhydrous methanolic sodium methoxide.

The reaction is not highly regioselective for unsymmetrical olefins. Styrene gives a single product (Markovnikov) but 1-methylcyclohexene and methyl acrylate give mixtures. In all cases that we have studied, the addition is stereospecific: *cis*- and *trans*-butenes give different adducts; cyclohexene gives a single adduct with both substituents equatorial.[9] Cyclohexadiene gives predominantly *trans*-1,2 addition; a small amount of a 1,4 adduct is formed under some conditions.[11]

This preparation of β-hydroxyalkyl phenyl selenides is synthetically equivalent to the sequence involving epoxidation and opening of the epoxide with phenylselenolate anion described by Sharpless and Lauer.[2a] Although both sequences involve introduction of hydroxyl and phenylseleno substituents in a trans fashion, complementary regioselectivity is anticipated and observed (*e.g.*, cyclohexadiene), since phenylselenolate is the nucleophile in the epoxide opening, and trifluoroacetate is presumably the 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$_2$CCF$_3$ in benzene gives **3** (stereochemistry assumed): 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$_2$CCF$_3$ 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$_2$CCF$_3$ 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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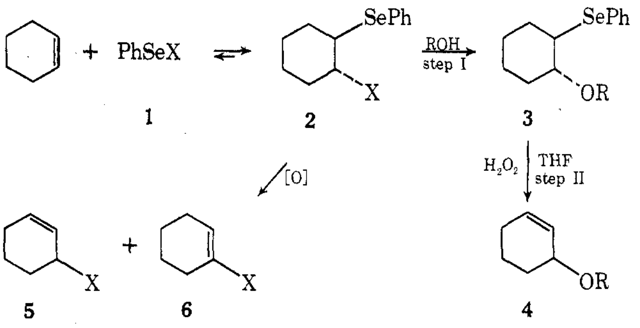
Electrophilic Organoselenium Reagents. A New Route to Allylic Acetates and Ethers

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$_2$O$_2$, 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$_2$O$_2$ was added over a 15-min period. After 20 min the cooling bath was removed and the solution allowed to warm. When the mixture