Reaction of Olefins with Benzeneselenenyl Bromide and Silver Trifluoroacetate: a New Method for Access to the Selenoxide Fragmentation Reaction

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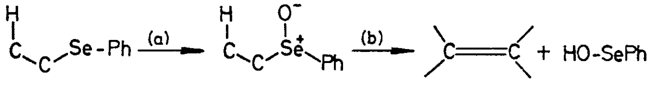
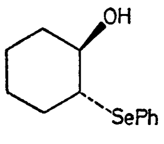
Summary Reaction of olefins at low temperature with benzeneselenenyl bromide and silver trifluoroacetate followed by treatment with sodium hydrogen carbonate produces β-hydroxy selenides, precursors to allylic alcohols.

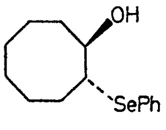
It has been recognised that selenoxide fragmentation [equation (1) stage (b)] constitutes a general method for introducing unsaturation into a carbon σ-bond system.[1] Both the oxidation, step (a), and the *in situ* fragmentation are efficient and they occur under gentle conditions with predictable[1c] *syn* stereochemistry for the fragmentation. The utility of this mild procedure in synthesis depends critically upon effective methods for introducing selenium as, for example, PhSe into substrate molecules.[1a] I report here that the active species formed from benzeneselenenyl bromide and silver trifluoroacetate† is sufficiently electrophilic to combine rapidly with unactivated olefins‡ at —10° to room temperature. Yields are high and very mild hydrolysis ($NaHCO_3$, H_2O) removes the trifluoroacetyl group incorporated by the process. The products (**1**)—(**4**), β-hydroxy selenides, are here formed with *trans*-stereochemistry (Table).



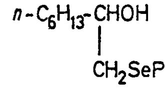
(1)



(1)

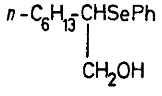


(2)



$$\begin{array}{l} n\text{-}C_6H_{13}\text{-}CHOH \\ \qquad\quad | \\ \qquad CH_2SePh \end{array}$$

(3)



$$\begin{array}{l} n\text{-}C_6H_{13}\text{-}CHSePh \\ \qquad\quad | \\ \qquad CH_2OH \end{array}$$

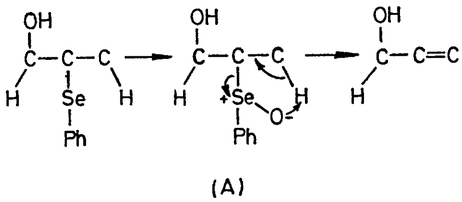
(4)

In the case of the terminal olefin, there is little regioselectivity but for symmetrical olefins the present method offers a gentle alternative to treatment of an epoxide with the strongly nucleophilic PhSe⁻, which is the previous route to β-hydroxy selenides.[1b] The importance of these compounds is due to the fact that oxidation converts[1b] them efficiently into allylic alcohols [equation (2)].§

Table

Olefin	Product	Yield (%)	Ref.
Cyclohexene	(**1**)	76	a,b
Cyclo-octene	(**2**)	72	b,c
Oct-1-ene	(**3**) (**4**)	87	a,b,d a,e

[a] Constitution defined by mass measurement. [b] Identical to specimen made[1b] from corresponding epoxide. [c] Differentiated from isomeric *cis*-compound[a] made by displacement (PhSe⁻) of halide from *trans*-2-hydroxycyclo-octyl bromide.[2] [d] Slight predominance of this isomer. [e] Reference sample made by reduction ($NaBH_4$) of corresponding α-phenylseleno-aldehyde.[a]



(2)

In a typical example of the present reaction, benzeneselenenyl bromide (1·2 equiv.) in anhydrous, peroxide-free, ether was added to a solution, kept at —10°, of the olefin (1 equiv.) and silver trifluoroacetate (1·4 equiv.) in the same solvent. The mixture was then allowed to warm to +20° during 2 h and the resulting *trans*-β-trifluoroacetoxy selenide[5] was hydrolysed in aq. methanolic $NaHCO_3$ at room temperature (*ca.* 3 h).¶

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† Benzeneselenenyl bromide itself reacts with olefins.

‡ For response of enol acetates to this reagent system see ref. 1a.

§ Fragmentation leading, for example, to enol or to unfunctionalised olefin [intramolecular attack of the hydroxy-group in (A) on selenium to produce a four-membered intermediate which expels benzeneseleninic acid[3]] have not been reported. The latter is a significant possibility with respect to the reaction of $PhSeCH_2Li$ with ketones.[4]

¶ *Cf.* A 16 h period at the reflux temperature of an n-butanol solution is recommended for the epoxide route in the cyclo-octyl ase.[1bc]

[1] (a) D. L. J. Clive, *J.C.S. Chem. Comm.*, 1973, 695; (b) K.B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, 1973, **95**, 2697; (c) K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Letters*, 1973, 1979; (d) H. J. Reich, I. L. Reich, and M. J. Renga, *J. Amer. Chem. Soc.*, 1973, **95**, 5813; (e) K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *ibid.*, 6137.

[2] J. G. Traynham and J. Schneller, *J. Amer. Chem. Soc.*, 1965, **87**, 2398.

[3] *Cf.* E. J. Corey and T. Durst, *J. Amer. Chem. Soc.*, 1966, **88**, 5656; F. Jung, N. K. Sharma, and T. Durst, *ibid.*, 1973, **95**, 3420.

[4] D. Seebach and N. Peleties, *Chem. Ber.*, 1972, **105**, 511; *cf.* also R. L. Sowerby and R. M. Coates, *J. Amer. Chem. Soc.*, 1972, **94**, 4758.

[5] *Cf.* G. Hölzle and W. Jenny, *Helv. Chim. Acta*, 1958, **41**, 593.