Conversion of Ketones into Lactones with Benzeneseleninic Acid and Hydrogen Peroxide (Benzeneperoxyseleninic Acid): a New Reagent for the Baeyer-Villiger Reaction

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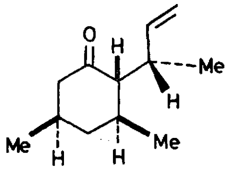
Summary Benzeneperoxyseleninic acid generated *in situ* from benzeneseleninic acid and hydrogen peroxide constitutes a new reagent for the Baeyer–Villiger reaction.

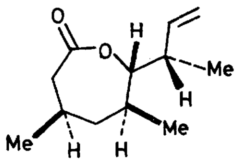
The ability of benzeneperoxyseleninic acid to epoxidize olefins has recently been reported.[1] We report herein that benzeneperoxyseleninic acid (**1**) constitutes a new reagent for use in the Baeyer–Villiger reaction. The reagent is generated *in situ* from the readily available benzeneseleninic acid[2] and an excess of 30% hydrogen peroxide [equation (1)]. The reaction can be carried out under either homogeneous [tetrahydrofuran (THF)] or heterogeneous (CH_2Cl_2) conditions. In general, 1·25 mol. equiv. of PhSe(O)OH and 10 mol. equiv. of 30% H_2O_2 are employed. In order to suppress hydrolysis to the corresponding hydroxycarboxylic acid, the reaction can be buffered at pH 7 with phosphate buffer.

$$\underset{}{PhSe(O)OH} + H_2O_2 \rightarrow \underset{(\mathbf{1})}{PhSe(O)OOH} \qquad (1)$$

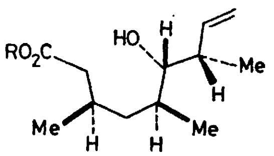
The following experimental procedure illustrates the method. A suspension of 1·25 mmol of PhSe(O)OH in 1·5 ml of CH_2Cl_2 and 1·0 ml of water was treated at room temperature with 10 mmol of *ca.* 30% aqueous H_2O_2. After 5 min, 1·0 mmol of 2-methylcyclohexanone in 1·0 m of CH_2Cl_2 was added to the vigorously stirred heterogeneous reaction mixture. The reaction was quenched after 1 h with saturated $NaHCO_3$ solution giving, after purification, pure lactone in 83% yield.



(2)



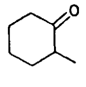
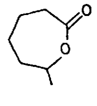
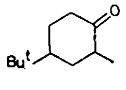
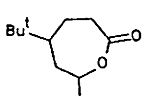
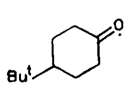
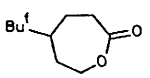
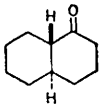
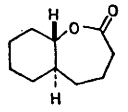
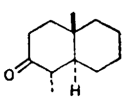
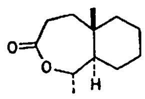
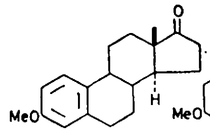
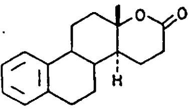
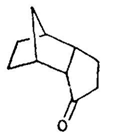
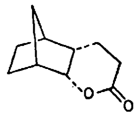
(3)



(4)
a; R = H
b; R = Me

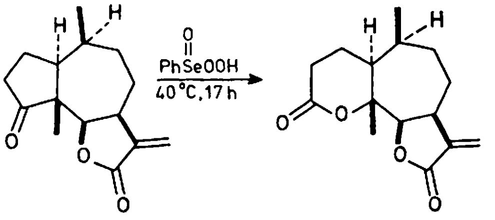
The potential of this new reaction was made evident from the Baeyer–Villiger oxidation of the ketone (**2**) which could not be oxidized to either the lactone (**3**) or the hydroxy acid (**4a**) employing a variety of procedures[3] (40% peroxyacetic acid, *m*-chloroperoxybenzoic acid, anhydrous peroxyacetic acid, and selenium dioxide–hydrogen peroxide). Initial attempts at oxidation of (**2**) with (**1**) [1·25 mol. equiv. PhSe(O)OH, 10 mol. equiv. 30% H_2O_2] in THF gave, after 4 h, a *ca.* 15% yield of (**3**) with 50% recovery of the starting ketone. However, heating the above reaction mixture for 13 h at 45 °C gave, after work-up and esterification, a 63% isolated yield of the pure hydroxy ester (**4b**).†

TABLE. Reaction of ketones with benzeneperoxyseleninic acid.[a]

Ketone	Product	Solvent	Time/h	% Yield[b]
		THF CH_2Cl_2	0.75 1	60[c] 83
		CH_2Cl_2	2	83
		CH_2Cl_2	18	67
		CH_2Cl_2	2.5	79[d]
		CH_2Cl_2	2	50[e]
		THF	24	80
		CH_2Cl_2	96	60[f]

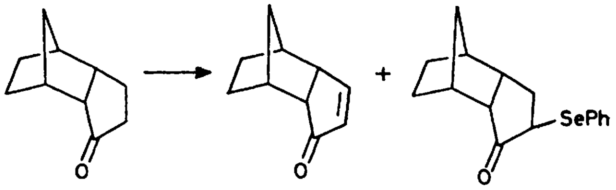
[a] All reactions were carried out in either THF or CH_2Cl_2, as indicated, using 1·25 mol equiv. of PhSe(O)OH and 10·0 mol. equiv. of 30% aqueous H_2O_2. [b] All compounds were fully characterized by spectral methods. Yields reported are for isolated, chromatographically pure substances. [c] *Ca.* 8% of the corresponding hydroxy acid isolated as its methyl ester was found. [d] This reaction was carried out in the presence of pH 7 phosphate buffer. [e] *Ca.* 45% of the starting ketone was recovered. [f] Starting material was recovered in 35% yield.

Cyclopentanones can be slowly converted into δ-lactones employing the conditions given in the Table. For example, estrone methyl ether gave the corresponding δ-lactone in 80% yield after 24 h. The synthesis of natural psilostachyin C from damsin was carried out [equation (2)] employing (**1**) [2·0 mol. equiv. PhSe(O)OH, 15 mol. equiv. 30% H_2O_2] in Bu^tOH. Natural psilostachyin C, m.p. 224—225 °C (lit.[4] m.p. 224—226 °C), was obtained in 55% isolated yield. *Ca.* 20% of the corresponding hydroxycarboxylic acid, which resulted from hydrolysis of the δ-lactone during the course of the reaction or the work-up, was isolated.



(2)

During an attempt to reduce the amount of H_2O_2 employed in the examples cited in the Table, we observed a novel reaction with the ketone (**5**). Upon treatment of (**5**) in THF with 1·25 mol. equiv. of PhSe(O)OH and 1·50 mol. equiv. of 30% H_2O_2, we isolated, after 16 h, a 60% yield of the pure enone (**6**) and a 12% yield of the keto selenide (**7**). There was no lactone formation under the above conditions.



(5) (6) (7)

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† This reaction was carried out by Dr. M. Uemura.

[1] P. A. Grieco, Y. Yokoyama, S. Gilman, and M. Nishizawa, *J. Org. Chem.*, 1977, **42**, 2034.
[2] J. D. McCullough and E. S. Gould, *J. Amer. Chem. Soc.*, 1949, **71**, 674.
[3] P. McCurry, personal communication.
[4] H. B. Kagan, H. E. Miller, W. Renold, M. V. Lakshimkantham, L. R. Tether, W. Herz, and T. H. Mabry, *J. Org. Chem.*, 1966, **31**, 1629.