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Stereoselective Selenolactonization by Superelectrophilic Benzeneselenenyl Triflate

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Benzeneselenenyl triflate is prepared from benzeneselenenyl chloride and silver trifluoromethanesulfonate. It performs selenium-induced cyclization of β,γ-, γ,δ-, and δ,ε-unsaturated carboxylic acids.

Olefin lactonization has been used for syntheses of complex molecules as an important tool for acyclic stereoselective introduction of oxygen functional groups.1) Selenolactonization and related reactions2) are particularly favorable for expansion of functional groups because the resulting selenolactone is convertible to the olefinic lactone. However, in the reaction of organoselenenyl halides,3-7) presence of the nucleophilic halide anion causes unfavorable actions such as addition of the halogen atom and decrease of the stereoselectivity. On the other hand, reactions of N-phenylselenoimides which are out of the effect of nucleophile require a strong acid catalyst because of their less reactivity.8,9) Described herein is preparation of highly electrophilic benzeneselenenyl triflate which does not have nucleophilic counter anion, a so-called superelectrophile, and its application for selenolactonization.

Preparation of benzeneselenenyl triflate (**1**, $PhSeOSO_2CF_3$ = PhSeOTf) from benzeneselenenyl chloride and silver trifluoromethaneslufonate was performed in dichloromethane or toluene and it could be used to the following reaction *in situ*. ^{13}C NMR,10) in which all signals appeared at lower chemical shifts than benzeneselenenyl chloride, suggested strong electrophilicity of **1**. Indeed, reaction of **1** with γ,δ-unsaturated carboxylic acids **2** proceeded even at -78 °C to give γ-lactones **3**, exclusively. When the starting material and product decompose by

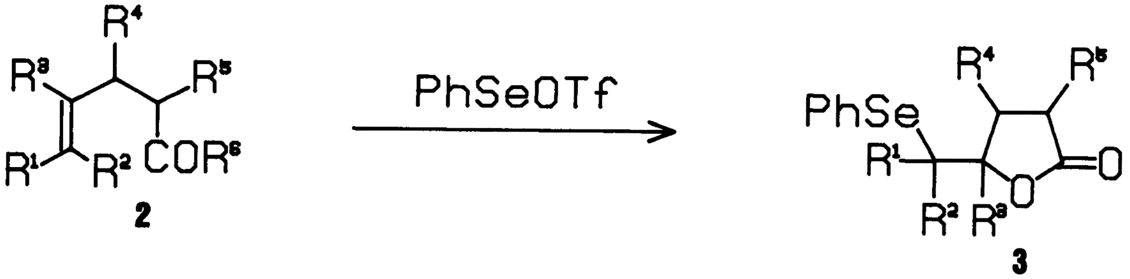
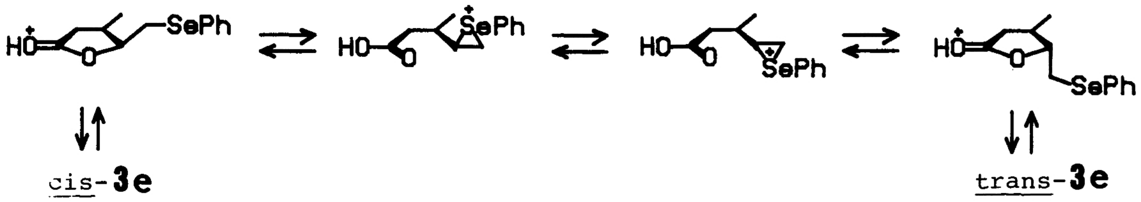


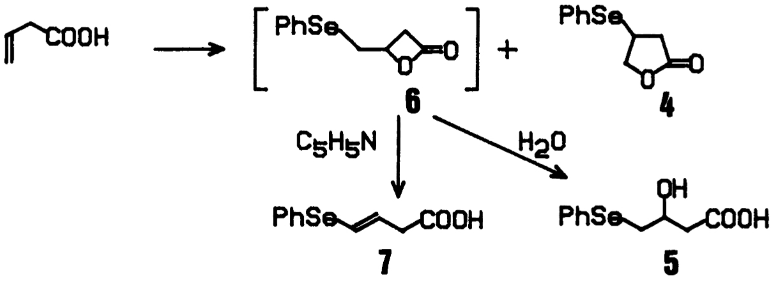
Table 1. Selenolactonization of γ,δ-Unsaturated Acid Derivatives 2 by Benzeneselenenyl Triflate (1)[a]

	Substituents of 2 and 3						3	
Substrate	R^1	R^2	R^3	R^4	R^5	R^6	Yield/%	trans/cis
2a	H	H	H	H	H	OH	83	
2b	CH_3	H	H	H	H	OH	88	
2c	CH_3	CH_3	H	H	H	OH	47[b,c]	
2d	H	H	CH_3	H	H	OH	91	
2e	H	H	H	CH_3	H	OH	83, 85[d]	10:1,[e] 5:4[d]
2f	H	H	H	H	CH_3	OH	85	4:3[f]
2g	H	H	H	CH_3	H	NH_2	49	5:1
2h	H	H	H	CH_3	H	OCH_3	73	14:1

a) Unless otherwise stated the reactions were carried out with 1.1 equivalent of 1 at 0 °C. b) A 1:1 mixture of 1 and pyridine was employed. c) A δ-lactone, 5-methyl-4-phenylseleno-5-hexanolide, was obtained in 29% yield. d) Reaction was carried out at -78 °C. e) Benzeneselenenyl chloride gave 1:1 mixture of trans- and cis-3**e**; see Ref. 7. f) Stereochemical structures were unknown.

trifluoromethanesulfonic acid formed during the reaction, addition of 1 equivalent of pyridine prevented these disadvantages. Formation of δ-lactone was recognized only in the 5,5-disubstituted substrate **2c** whose δ-position was activated as tertiary cationic center in the intermediate. Since there seems to exist the thermodynamic equilibrium between cis- and trans-isomers of **3e** at 0 °C, reaction of 3-methyl-4-pentenoic acid (**2e**) gave the stable isomer trans-**3e** stereoselectively. However the reaction did not attain equilibrium at -78 °C, and produced trans- and cis-**3e** unselectively. The isomer ratios were determined by 270 MHz ^{1}H NMR and their structures were confirmed by derivation (Bu_3SnH/AIBN/toluene)[8] to authentic trans- and cis-3-methyl-4-pentanolides.[11] An amide **2g** and ester **2h**





were also converted into the γ-lactone **3e**. The results are summarized in Table 1. Reaction of **1** with 3-butenoic acid which underwent addition of chloride ion by the reaction with benzeneselenenyl chloride[5,6] gave a mixture of 3-phenylseleno-4-butanolide (**4**, 29% at 0 °C, 11% at -78 °C) and 3-hydroxy-4-phenylselenobutanoic acid (**5**, 16% at 0 °C, 58% at -78 °C). The latter compound was probably formed by hydrolysis of the β-lactone **6** by the aqueous work-up and/or silica-gel column. When 3-butenoic acid was treated with 1:1 mixture of **1** and pyridine at 0 °C, E-4-phenylseleno-3-butenoic acid **7** (19%), which seemed to be derived from **6** by pyridine-induced ring opening, was obtained together with trace amounts of **4** and **5**.[12] 5-Hexenoic acid was converted exclusively into 6-phenylseleno-5-hexanolide in 86% yield.

The following experiment is representative. To a solution of benzeneselenenyl chloride (0.56 g, 2.8 mmol) in CH_2Cl_2 (30 ml) was added silver trifluoromethane-slufonate (0.72 g, 2.8 mmol) at 0 °C. After the mixture was stirred for 10 min, benzeneselenenyl triflate (**1**) was obtained as a pale orange suspension. To this was added 3-methyl-4-pentenoic acid (0.29 g, 2.5 mmol) at 0 °C. The mixture was stirred for 1 h and was diluted with ether (100 ml). After concentration *in vacuo*, column chromatography on silica gel eluting with CH_2Cl_2 gave a 10:1 mixture of *trans*- and *cis*-5-phenylseleno-3-methyl-4-pentanolides (0.56 g, 83% yield).

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10) ^{13}C NMR ($CDCl_3$) δ130.6 (two signals), 132.8, and 135.1.

11) The authentic trans- and cis-3-methyl-4-pentanolides were prepared respectively by reductive deiodation (Bu_3SnH/AIBN/toluene 110 °C) from trans- and cis-5-iodo-3-methyl-4-pentanolides which were obtained by iodolactonization of 3-methyl-4-pentenoic acid; see: P. A. Bartlett and J. Myerson, J. Am. Chem. Soc., 100, 3950 (1978).

12) This and the following results suggested the formation of **6**. Since the reaction of trans-cinnamic acid or cyclohexene with **1** under presence of pyridine at 0 - 35 °C did not give the corresponding alkenyl phenyl selenide, **7** might not be formed via addition of **1** to the carbon-carbon double bond followed by β-elimination of trifluoromethanesulfonic acid.

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