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STEREOSELECTIVE FORMATION OF TETRAHYDROFURAN AND -PYRAN BY BENZENESELENENYL TRIFLATE

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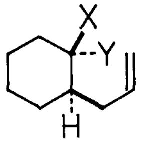
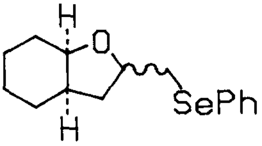
Summary: Cyclization of *cis*- and *trans*-2-allylcyclohexanols and cyclohexene-3-yl alcohols with benzeneselenenyl triflate affords corresponding fused tetrahydrofurans and -pyrans.

There have been known several interesting marine natural polyethers which are consisted of fused cyclic ethers.[1] Although intramolecular oxyselenation of an olefinic alcohol seems to be an useful technique for construction of cyclic ethers with various functional groups, stereoselective formation of fused tetrahydrofuran and -pyran systems has not been achieved by this method.[2] Described herein is a basic study on syntheses of those fused ring ethers by superelectrophilic benzeneselenenyl triflate (**1**).[3]

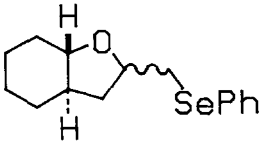
Reaction of *cis*-2-allylcyclohexanol (**2a**)[4] with **1** at 0 °C in dichloromethane proceeded to give 8-phenylselenomethyl-*cis*-7-oxabicyclo[4.3.0]nonane (**3a**).[5] On the contrary, *trans*-isomer **2b**[4] was selectively converted to 4-phenylseleno-*trans*-2-oxabicyclo[4.4.0]decane (**4b**) under the same condition, but 5-*endo*-cyclization of **2b** occurred predominantly to give **3b**[5] under the following condition: at -78 °C or with pyridine at 0 °C. Reactions of 2-cyclohexen-3-yl-ethanol (**5**) and 3-cyclohexen-3-yl-propanol (**6**) with **1** gave 5-phenylseleno-*cis*-7-oxabicyclo[4.3.0]nonane (**3c**) and 10-phenylseleno-*cis*-2-oxabicyclo[4.4.0]decane (**4c**), respectively. Results are summarized in Table 1.



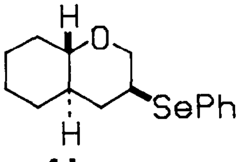
2a **2b**



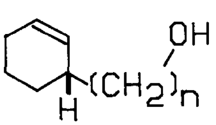
3a



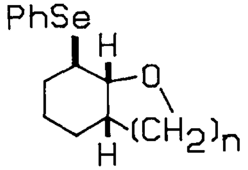
3b



4b



5 **6**



3c **4c**

2a: X = OH, Y = H; **2b**: X = H, Y = OH; **5**, **3c**: n = 2; **6**, **4c**: n = 3

Table 1. **Benzeneselenenyl Triflate (1) Induced Cyclization**

substrate	conditions temp./°C	 additive	product (yield/%)
2a	0	none	**3a** (83)
2a	0	C_5H_5N	**3a** (52)
2b	0	none	**3b** (84), **4b** (5)
2b	-78	none	**3b** (8), **4b** (79)
2b	0	C_5H_5N	**3b** (45)
5	0	none	**3c** (90)
6	0	none	**4c** (68)

The reaction seemed to proceed via intramolecular nucleophilic attack of OH group toward an olefin-$PhSe^+$ π complex, and this type of ring formation would usually afford an exo-cyclized product.[6] Since there were not any nucleophilc nor basic species except triflate ion in the reaction mixture, reaction of **2b** with **1** seemed easy to attain the equilibrium between the substrate and products (**3b** and **4b**) even at 0 °C. Formation of **4b**, the 6-endo-cyclization, proceeded under the thermodynamic control,[7] but presence of the base (pyridine) could quench the equilibrium to give the kinetic product (**3b**).[7] The following result is an evidence for the existence of the equilibrium: When **3b** was treated with 1 eq. of trifluoromethaneslufonic acid in CH_2Cl_2 at 0 °C for 5 min, a mixture of **3b** and **4b** was obtained in 82:18 ratio.

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