NOVEL CYCLIZATION OF UNSATURATED ALCOHOLS BY PHENYL SELENOCYANATE IN THE PRESENCE OF COPPER BIS(TRIFLUOROMETHANESULFONATE)

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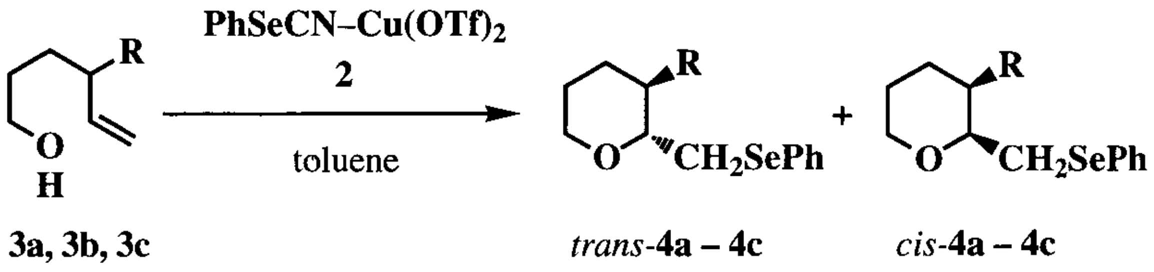
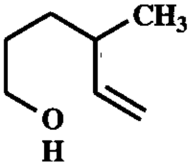
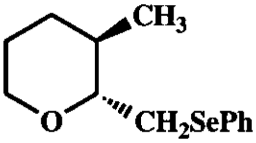
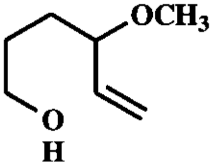
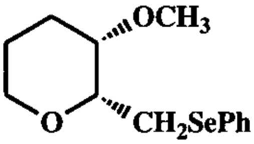
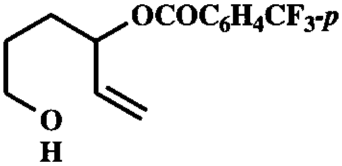
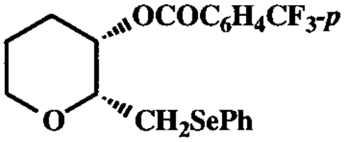
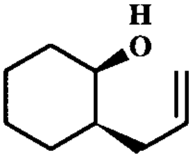
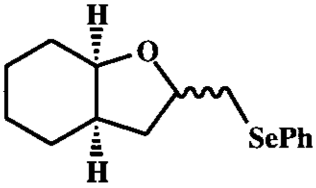
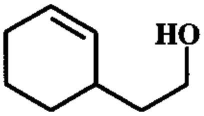
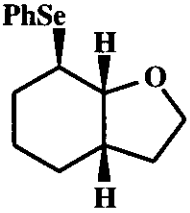
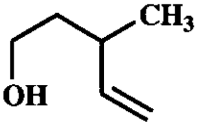
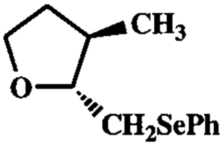
Abstract–Intramolecular oxyselenenylation of unsaturated alcohols by phenyl selenocyanate with copper bis(trifluoromethanesulfonate) proceeds stereoselectively to give cyclic ethers.

Organic selenocyanates, which have been known for more than 100 years, are very stable compounds and can be widely prepared from the corresponding organohalogen compounds or aromatic amines by simple substitution reactions using potassium selenocyanate and so on.[2] In addition, it is very easy to convert the –SeCN group into other selenium functional groups.[2,3] Therefore, aryl selenocyanates have been generally employed as fundamental precursors for various organoselenium nucleophiles such as $ArSe^-$.[2–4] In the contrast, there were only a few examples of aryl selenocyanates which were activated by Lewis acids or metal salts (Cu^{2+} or Ni^{2+}) as an electrophilic organoselenium reagent in organic synthesis.[5–9] In this communication, we describe about preparation of a new electrophilic reagent from phenyl selenocyanate (**1**) and copper bis(trifluoromethanesulfonate) ($Cu(OTf)_2$)[10] and its application to regio- and stereoselective cyclization of unsaturated alcohols.



3a, **4a**: R = CH_3; **3b**, **4b**: R = OCH_3; **3c**, **4c**: R = $OCOC_6H_4CF_3$-*p*

Table 1. Cyclization of Unsaturated Alcohols (3) by PhSeCN–Cu(OTf)$_2$ (2).

unsaturated alcohol **(3)**	cyclic ether **(4)** (yield/%)	
		(95)[b]
		(78)[c]
		(78)[d]
 **3d**	 **4d**	(73)
 **3e**	 **4e**	(88)
 **3f**	 **4f**	(85)[e]

[a] Isolated yield after silica gel column chromatography. [b] *trans/cis* = 96:4. [c] *trans/cis* = 13:87. [d] *trans/cis* = 23:77. [e] *trans/cis* = 89:11.

The reagent (PhSeCN–Cu(OTf)$_2$, **2**) was obtained from a 1:1 mixture of **1** and Cu(OTf)$_2$ in toluene (at 50 °C) or dichloromethane (under reflux) as a yellowish brown suspension.

Reactions of 4-methyl-5-hexen-1-ol (**3a**) and the 4-methoxy and 4-*p*-trifluoromethylbenzoyloxy analogs (**3b** and **3c**, respectively) with **2** proceeded at 25 ˚C to give *trans*-2-phenylselenomethyl-3-methyltetrahydoropyran (*trans*-**4a**, 95% yield; 96:4 selectivity), *cis*-**4b** (78%; *trans/cis* = 13:87), and *cis*-**4c** (78%; *trans/cis* = 23:77) as major products, respectively. The results of cyclization of unsaturated alcohols (**3a** – **3f**) by **2** are summarized in Table 1. There, *exo*-cyclized 5- and 6-membered ring ethers (**4a** – **4f**) were regioselectively obtained in high yields. Existence of either *endo*-cyclized products or nitriles resulting from the cyanoselenenylation[6] was not detected in the crude reaction mixtures. The exo selectivity and stereoselectivities depending on substituents at the allylic position were almost same as reactions which were carried out by benzeneselenenyl trifluoromethanesulfonate (PhSeOTf),[11–15] and yields of **4** were better than those in reactions using PhSeOTf.

It was known that organic selenocyanate (RSeCN) was converted into selenenyl halide (RSeX) by a metal salt (CuX_2 or AgX),[16] and formation of PhSeOTf by the same mechanism was likely to occur. However, the reactivity of **2** toward **3** was lower than that of typical PhSeOTf prepared from PhSeCl and AgOTf. For example, the trans isomer of **3d** (*trans*-2-allylcyclohexanol) which was smoothly cyclized by PhSeOTf even at -78 ˚C[13] did not react with **2** in the same conditions. And even in the presence of trifluoromethanesulfonic acid, oxyselenenylation of **3a** to **4a** by **1** has not proceeded. Thus, we suppose that the reagent (**2**) contains a highly electrophilic organoselenium complex of copper. Mechanisms of stereoselectivities of **4a**, **4b**, **4c**, and **4f** were explained by the steric repulsion (**4a** and **4f**: trans predominating) and the electronic attraction (**4b** and **4c**: cis predominating) between the allylic substituent (R) and electropositive Se atom in 3-membered ring cationic seleniranium intermediates.[15,17–19]

The following is a typical example of the reaction of **3** with **2**: A mixture of $Cu(OTf)_2$ (0.36 g, 1.0 mmol) and **1** (0.18 g, 1.0 mmol) in toluene (3.5 mL) was stirred at 50 ˚C for 1 h. To the resulting suspension was added **3a** (0.10 g, 0.90 mmol) at 25 ˚C, and the mixture was stirred for 1 h. To this was added saturated $NaHCO_3$ (3 mL) and dichloromethane (15 mL), and precipitate was removed by a centrifuge. The organic solution was concentrated, and the residue was subjected to silica gel column chromatography eluting with 5% (*v/v*) ethyl acetate in petroleum ether. A 96:4 mixture of *trans*-**4a** and *cis*-**4a** was obtained as pale yellow oil (0.23 g, 95% yield). Spectroscopic and analytical data of the products were listed in the reference.[15]

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