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PHENYLSELENENYL CHLORIDE AS A REAGENT FOR THE FACILE PREPARATION OF CYCLIC ETHERS FROM DIOLEFINS

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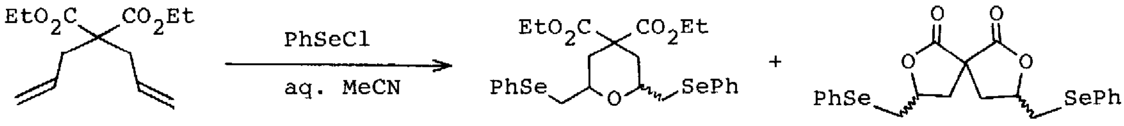
Summary: Various cyclic ethers are prepared in good to excellent yields by treating diolefins with phenylselenenyl chloride in aqueous acetonitrile. This is the most facile method for organoselenium-induced formation of cyclic ethers from diolefins so far reported.

We have recently reported that the treatment of diolefins with phenyl selenocyanate and copper(II) chloride in hydroxylic solvents resulted in the formation of cyclic ethers containing two phenylseleno groups.[1,2] Nicolaou *et al.* have also reported similar cyclization reaction by using N-phenylselenophthalimide, N-phenylselenosuccinimide, or "PhSeOH".[3,4] Although these methods are very efficient for the preparation of cyclic ethers, it is still necessary to use the catalyst such as metal salt or acid, to carry out the reaction under anhydrous condition under argon, and/or to prepare effective phenylselenenyl reagents from various selenium compounds. During the attempts to overcome these disadvantages we have now found that the reaction of diolefins with commercially available phenylselenenyl chloride in aqueous acetonitrile afforded similar products in good to excellent yields. This seems to be the first example for the use of phenylselenenyl chloride in aqueous solvent. This reagent has so far been known to be very hygroscopic and therefore believed to be unstable in water.

A typical experimental procedure is as follows. To a solution of phenylselenenyl chloride(10 mmol) in aqueous acetonitrile($MeCN:H_2O=5:1$, 18 ml) was added 1,5-hexadiene(5 mmol) and the mixture was stirred at 76°C for 5 h. After quenching the reaction by the addition of aqueous $NaHCO_3$, the mixture was extracted with chloroform and the extract was washed with aq. NaCl and dried over $MgSO_4$. Chloroform was then removed and the residue was subjected to column chromatography(silica-gel; hexane-ethyl acetate as eluent) to afford a mixture of 2,5-bis(phenylselenomethyl)-1-oxacyclopentane (2) and 2-phenylselenomethyl-5-phenylseleno-1-oxacyclohexane (2') in 90% yield[(2):(2')=90:10] (See Table). The reactions of other several diolefins were similarly carried out to give the corresponding cyclic ethers, (1)-(9'), in comparable or better yields to or than those reported.[1-4] The structure of these products was determined by ^{13}C- and ^{1}H-NMR, IR, and mass spectra, and elemental analysis, the isomer ratio being determined by liquid chromatography (column; μ-Porasil 3.9 mm x 30 cm). ^{13}C-NMR spectra and liquid chromatography revealed that each of (1), (2), (5), (6), and (7) consisted of nearly equal amounts of two stereoisomers, probably *cis* and *trans* with respect to two phenylselenomethyl substituents or one phenylselenomethyl and one phenylseleno moiety.

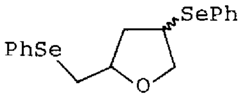
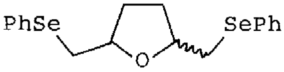
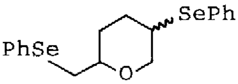
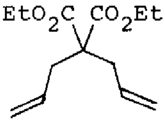
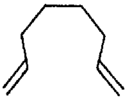
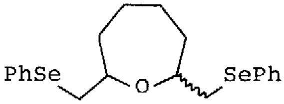
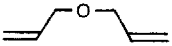
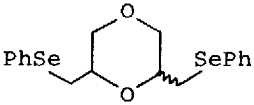
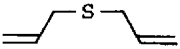
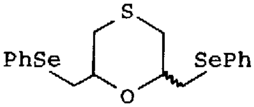
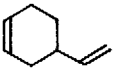
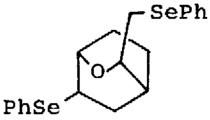
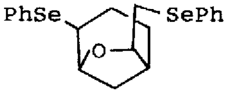
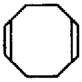
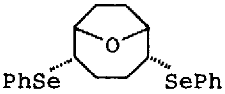
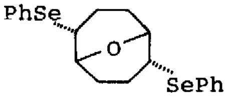
From diethyl diallylmalonate a good yield of spiro-bislactone (4) was obtained together with the expected cyclic ether (3). It was revealed by



(3) (4)

^{13}C-NMR spectra that (3) and (4) consisted of two stereoisomers(*ca*. 3:1) and three isomers(*ca*. 2:3:5), respectively. Since we confirmed separately that no isomerization between (3) and (4) occurred under the present reaction conditions, (3) and (4) should be formed in different routes. Although organoselenium-induced intramolecular lactonization of olefinic carboxylic acid has been known,[5] the present result seems to be the first example for such phenylselenolactonization from carboxylic ester. The scheme such as the hydrolysis of ester to give a free dicarboxylic acid which is followed by lactonization to give (4) may be ruled out, since no hydrolyzed compound of (3)[mono- or dicarboxylic acid of (3)] was detected in the products.

TABLE Several cyclic ethers by oxyselenation of diolefins[a)]

Diolefin	Temp. (°C)	Time (h)	Products	Yield(%)[b)] (Product ratio)[b)]
	76	5	 (1)	50[c)]
	76	5	 (2) +  (2')	90 (90:10)
	76	5	(3) + (4)	97 (42:58)[c)]
	25	5		96 (50:50)[c)]
	76	5	 (5)	34
	76	24	 (6)	66
	76	24	 (7)	55
	76	5	 (8) +  (8')	70 (84:16)[d)]
	76	24	 (9) +  (9')	94 (3:97)
	25	24		92 (88:12)

a) Diolefin (1 mmol), PhSeCl (2 mmol), and aq.MeCN (3.6 ml; MeCN:H_2O = 5:1) were used. b) Determined by liquid chromatography. c) Isolated yield and the ratio of the isolated products. d) Assignment for two products might be reversed

Another interesting feature of the present method is found in the isomer ratio of (9) to (9') from 1,5-cyclooctadiene. We have already reported[1] the solvent-controlled selective formation of either (9) or (9') by oxyselenation with PhSeCN/$CuCl_2$ system; *i.e.*, aqueous tetrahydrofuran or methyl alcohol prefers the formation of (9) or (9'), respectively. By the present method, on the other hand, the formation of (9) or (9') can be controlled simply by changing the reaction temperature; namely, as shown in Table, (9) or (9') was the predominant product at 25°C or 76°C, respectively, (9') being a thermodynamically stable product.

The reaction seems to proceed *via* addition of phenylselenenyl chloride to one double bond, followed by hydrolysis, to give a β-hydroxyselenide which subsequently undergoes cyclization with participation of another phenylseleno moiety. The direct addition of phenylselenenic acid(PhSeOH), which may be formed *in situ*, to one double bond, however, can not be ruled out as the first step.

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