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FACILE PREPARATION OF CYCLIC ETHERS BY OXYSELENATION OF DIOLEFINS

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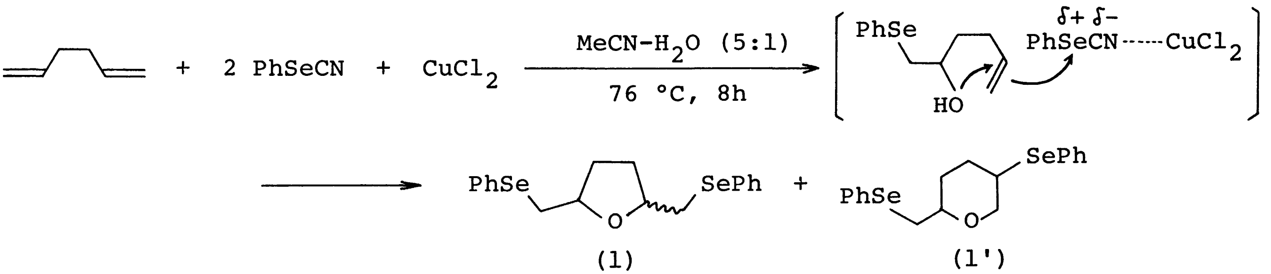
Reaction of several diolefins with phenylselenocyanate and copper(II) chloride in aqueous acetonitrile afforded various cyclic ethers having two phenylseleno groups in 42-88% yield. Hydroxyselenation of one double bond, followed by intramolecular oxyselenation on the other double bond, seems to be the reaction pathway.

We are currently interested in organoselenium chemistry from the viewpoint of organic synthesis[1)] and have reported quite recently the solvent-controlled formation of 9-oxabicyclo[3.3.1]nonane and -[4.2.1]nonane derivatives from 1,5-cyclooctadiene by oxyselenation in methyl alcohol and aqueous tetrahydrofuran.[2)] Recent reports by Nicolaou et al.[3)] on organoselenium-induced formation of cyclic ethers from diolefins prompted us to report our results on heterocyclization of several diolefins by copper-salt catalyzed oxyselenation.

A homogeneous mixture of 1,5-hexadiene(5 mmol), phenyl selenocyanate(10 mmol), and copper(II) chloride(5 mmol) in aqueous acetonitrile(MeCN:H_2O = 5:1, 18 ml) was stirred at 76 °C for 24h. After usual work-up procedure, a mixture of 2,5-bis-(phenylselenomethyl)-1-oxacyclopentane (1) and 2-phenylselenomethyl-5-phenylseleno-1-oxacyclohexane (1') was isolated in 84% yield [(1):(1') = 93:7] by column chromatography (silica gel; hexane—ethyl acetate as eluent). Similar reaction of diallyl ether, diallyl sulfide, 4-vinylcyclohexene, or 1,5-cyclooctadiene afforded the corresponding cyclic ethers, (2)~(5), in good to excellent yields. Typical results are shown in Table. The structural determination of all these products was carried out mainly by ^{13}C-NMR together with ^{1}H-NMR, IR, and elemental analysis, the isomer ratio being determined by liquid chromatography (column; μ-Porasil 3.9 mm x 30 cm). ^{13}C-NMR spectra revealed that each of (1), (2), and (3) consisted of nearly equal amounts of two stereoisomers, probably *cis* and *trans* with respect to the two phenylselenomethyl substituents: i.e., δ(ppm), (1); 78.4(d) and 79.0(d) for -$\underline{C}$HO-, (2); 69.7(d) and 74.9(d) for -$\underline{C}$HO-, (3); 70.4(d) and 78.4(d) for -$\underline{C}$HO-.

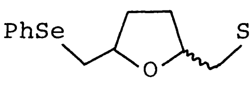
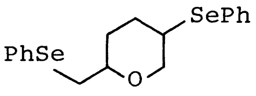
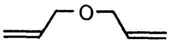
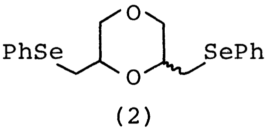
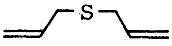
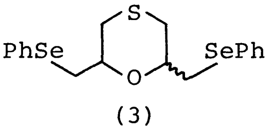
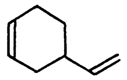
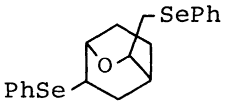
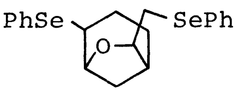
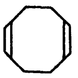
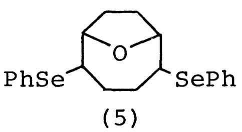
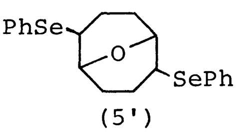


(1) (1')

The reaction proceeded in *t*-butyl alcohol as well, but the yields of the expected products were very low owing to formation of tarry products. In methyl alcohol, cyclization did not occur for 1,5-hexadiene and diallyl ether, only methoxyselenation products of two double bonds being formed.

As illustrated in the scheme, the reaction in aqueous acetonitrile seems to proceed as follows; hydroxyselenation of one double bond as the first step which is followed by *in situ* intramolecular alkoxyselenation of the other double bond.

Table. Formation of heterocyclic compounds by oxyselenation of diolefins[a]

Diolefin	Temp. (°C)	Time (h)	Products			Yield(%)[b] (Product ratio)[b]
	76	8	 (1)	+	 (1')	86 (91: 9)
〃	30	96				49 (90:10)
	76	24	 (2)			64
	76	24	 (3)			42
	76	8	 (4)	+	 (4')	43 (96: 4)[c]
	76	5	 (5)	+	 (5')	88[d] (44:56)
〃	30	96				88[d] (88:12)

a) Diolefin (1 mmol), PhSeCN (2 mmol), $CuCl_2$ (1 mmol), and aq. MeCN (3.6 ml; $MeCN:H_2O$ = 5:1) were used. b) Determined by liquid chromatography. c) Assignment for (4) and (4') might be reversed. d) Isolated yield.

References

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