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ELECTROCHEMICAL CYCLIZATION OF UNSATURATED HYDROXY COMPOUNDS.
PART I. PHENYLSELENOETHERIFICATION

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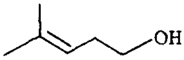
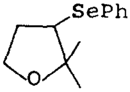
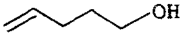
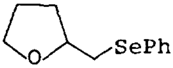
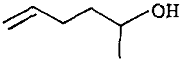
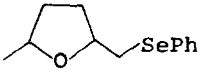
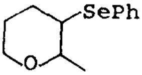
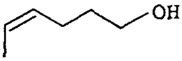
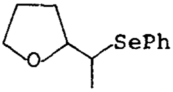
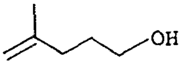
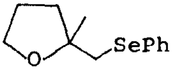
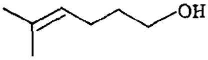
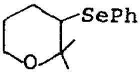
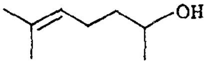
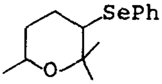
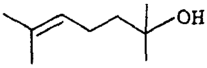
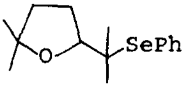
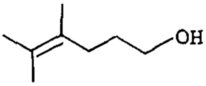
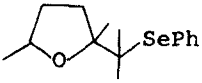
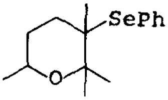
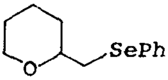
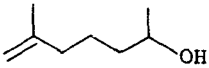
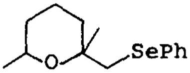
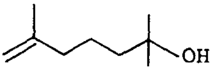
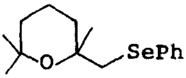
Abstract: One-step cyclization of alkenols has been accomplished by electrooxidative phenylselenoetherification. The reaction was performed by electrolysis of unsaturated alcohols and diphenyl diselenide in methylene chloride containing tetraethylammonium bromide.

The cyclization of unsaturated hydroxy compounds with phenylselenenyl chloride (PhSeCl), termed phenylselenoetherification, became an important tool for the synthesis of different natural products containing tetrahydrofuran and tetrahydropyran systems[1-3]. On the other hand, the oxyselenenylation-oxidative deselenenylation sequence provides double-bond transpositioned allylic alcohols and ethers from olefins[4], the usual procedure involving treatment with PhSeX (X = Cl, Br, OR, and NR_2) followed by oxidation with O_3, $NaIO_4$, and peroxides (H_2O_2, t-BuOOH, m-CPBA). Oxyselenenylation of olefins may be also performed by electrochemical oxidation of these substrates in the presence of diphenyl diselenide and halides as mediators in a water-acetonitrile medium[5-7].

We wish to report here our preliminary results on the transformation of olefinic alcohols to the corresponding cyclic phenylselenoethers by electrochemical oxidation. When alkenols (such as 4-penten-1-ol, 5-hexen-1-ol and their various substituted derivatives) and diphenyl diselenide were electrolyzed in cold methylene chloride solution in the presence of tetraethylammonium bromide as an electrolyte, phenylselenoethers were obtained in good to very good yields (50-86%). This methodology is illustrated as shown below, by using 5-hexen-1-ol as an example.

The electrolysis was performed in an undivided cell, using a graphite stick as an anode and Cu foil as a catode. A typical electrolysis procedure is as follows: A solution of 5-hexen-1-ol (100 mg; 1 mmol), diphenyl diselenide (156 mg; 0.5 mmol) and Et_4NBr (210 mg; 1 mmol) in methylene chloride (5 ml) was electrolyzed in a cell placed in an ice-acetone-salt bath (constant current 250 mA; 2 F/mol). When the reaction was completed, the solvent was distilled

Table. Electrochemical cyclization of unsaturated alcohols

Alcohol	mmol ROH	Products	Yield, %
	1.85		72
	1.16		80
	2.71		61[a]
	1.51		77[a]
	1.39		86
	0.48		79
	0.70		61
	1.63		67[a]
	0.48		50
	1.60	 +  (1:1)	52[a]
	1.00		75[a]
	1.60		75
	2.93		76

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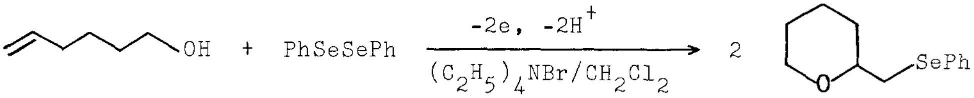
[a] The stereochemistry of these products was not, as yet, investigated.



off and the residue extracted several times with n-hexane. After removing n-hexane, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2), whereby 2-phenylselenomethyltetrahydropyran (199 mg; 75%) was isolated in the form of a pale yellow oil (Table).

The results obtained, given in the Table, can be summarized as follows. 3-Buten-1-ol did not cyclize under these conditions, but the simplest terminally disubstituted Δ^3-alkenol, 4-methyl-3-penten-1-ol, gave the corresponding five-membered cyclic ether, as the sole reaction product, in very good yield (72%). All the studied Δ^4- and Δ^5-alkenols afforded exclusively cyclic phenylselenoethers of the tetrahydrofuran- and/or tetrahydropyran-type as reaction products. The results obtained show also that the substituents at the double bond and carbinol carbon atom have a pronounced influence on the regioselectivity of ring closure, i.e. on the relative proportions of the five-membered and six-membered cyclic phenylselenoethers formed. In the case of Δ^4-alkenols with a terminally monosubstituted olefinic double bond of the Z-type, such as (Z)-4-hexen-1-ol, only the five-membered cyclic phenylselenoether was obtained, whereas the E-isomer, i.e., (E)-4-hexen-1-ol, gave exclusively the six-membered cyclic ether. Δ^4-Alkenols with a terminally dimethyl-substituted double bond, such as the primary 5-methyl-4-hexen-1-ol and secondary 6-methyl-5-hepten-2-ol, afforded six-membered cyclic phenylselenoethers, whereas the tertiary 2,6-dimethyl-5-hepten-2-ol was converted to the corresponding cyclic phenylselenoether (probably for stereochemical reasons). However, when the double bond is tetrasubstituted, as in the secondary 5,6-dimethyl-5-hepten-2-ol, both the five- and six-membered cyclic selenoethers are obtained.

5-Hexen-1-ol and substituted Δ^5-alkenols afforded exclusively tetrahydropyran-type phenylselenoethers.

Mild conditions (neutral medium and low temperature), simple equipment and inexpensive reagents are major advantages of this reaction for its application in the synthesis of O-heterocycles, particularly since the cyclic phenylselenoethers obtained can be readily deselenenylated and converted to other useful products[1-4].

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