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Electrochemical Oxyphenylselenation of Dienes

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Summary. The electrochemical oxidation of diphenyl diselenide in the presence of dienes affords the corresponding cyclic β-phenylselenoethers *via* an oxyphenylselenation process. The yields of ethers depend on the nature of the diene and on the reaction temperature.

Keywords. Dienes; Oxyphenylselenation; β-Phenylselenoethers; Tetrahydrofurans; Tetrahydropyrans.

Elektrochemische Oxyphenylselenierung von Dienen

Zusammenfassung. Die elektrochemische Oxidation von Diphenyldiselenid in Gegenwart von Dienen ergibt über einen Oxyphenylselenierungsprozeß die entsprechenden cyclischen β-Phenylselenoether. Die Ausbeuten an Ethern hängen von der Natur des Diens und der Reaktionstemperatur ab.

Introduction

The anodic generation of electrophilic selenium species in the presence of suitable substrates like carbonyl compounds, olefins, unsaturated alcohols, and carboxylic acids *etc*. has become a neat method for the introduction of selenium units into organic molecules. The application of this method in the synthesis of α-phenylselenoketons [1], aliphatic and cyclic β-phenylselenoethers [2, 3], β-phenylselenolactones [3] *etc*. has appeared in the literature. In continuation of our investigations directed at developing syntheses of oxygen containing heterocycles [3, 4], we subjected dienes to a treatment with the phenylselenyl cation derived from the electrochemical oxidation of diphenyl diselenide, expecting the formation of the corresponding cyclic ethers. These expectations were based on literature data describing oxyselenation induced by reagents such as PhSeOH [5], phenyl selenocyanate [6], and phenylselenyl chloride [7].

Results and Discussion

In the present investigation we started from the electrolysis of an acetic acid/water solution (10:1) of 1,5-cyclooctadiene (**1a**), diphenyl diselenide, and tetraethylam-

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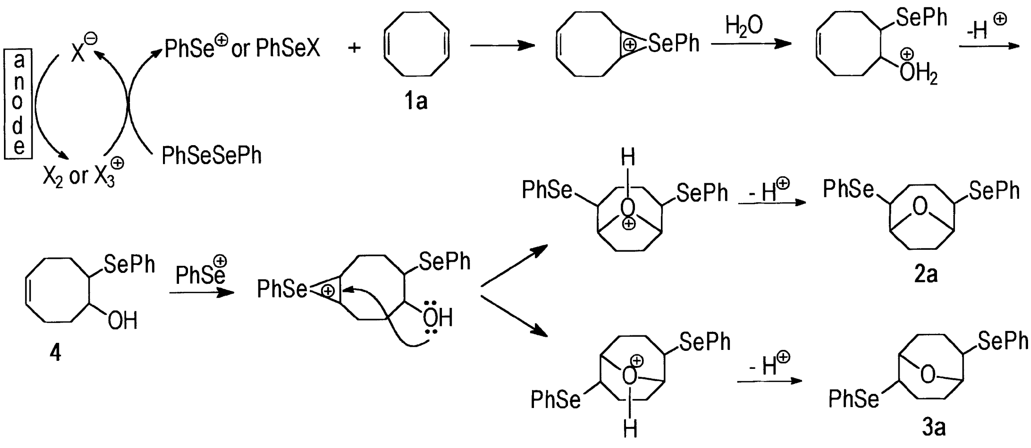
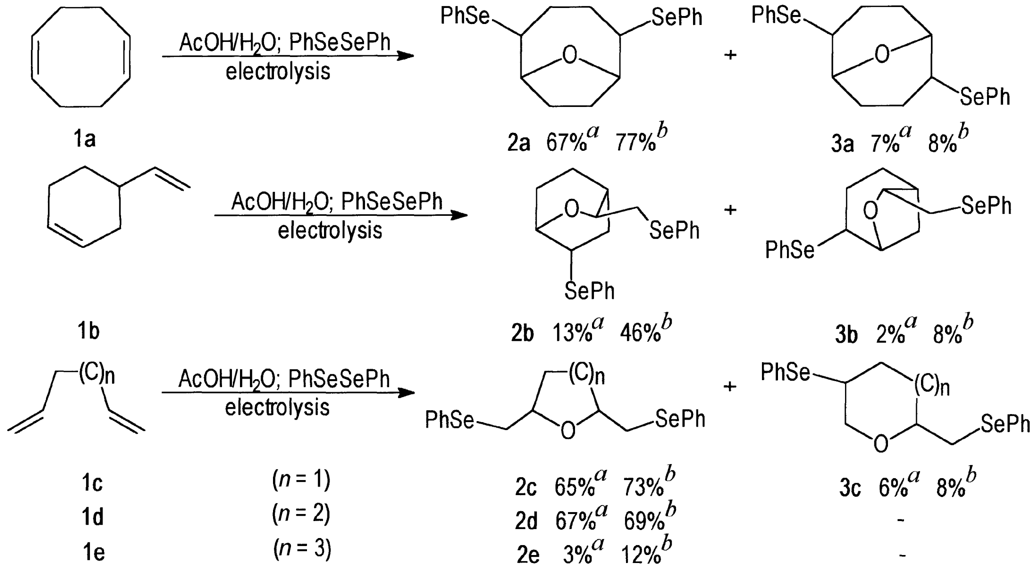


Scheme 1

monium chloride or bromide at a constant current (4 F/mol). From the reaction mixture, two selenosubstituted isomeric oxabicyclononanes, *i.e.* 2,5-*bis*(phenylseleno)-9-oxabicyclo[4.2.1]nonane (**2a**) and 2,6-*bis*(phenylseleno)-9-oxabicyclo-[3.3.1]nonane (**3a**) were isolated and identified by their IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data. When the reaction was carried out at ambient temperature, the total yield of these compounds was 74%; electrolysis under reflux resulted in a yield of 85%. However, in both cases ether **2a** was found to be the predominant one (**2a**/**3a** = 90:10 and 92:8).

We believe that the reaction starts by oxidation of halide ions at the anode to elemental halogens or halonium ions which then oxidize diphenyl diselenide, affording the phenylselenyl halide or the free phenylselenyl cation. These selenium species react with one of the double bonds of the diene, giving an episelenonium ion which attacks of the nucleophile water, affording the selenosubstituted unsaturated alcohol **4**. The reaction then proceeds further on the known way [3], affording ethers **2a** and **3a** (Scheme 1).

We applied this reaction technique to the oxyphenylsenation of another four dienes in order to synthesize the corresponding cyclic ethers. Thus, 4-vinylcyclohexene (**1b**), 1,5-hexadiene (**1c**), 1,6-heptadiene (**1d**), and 1,7-octadiene (**1e**) were subjected to electrolysis under the same conditions. The results are summarized in Scheme 2. As it can be seen from Scheme 2, the yield of the corresponding ethers depends on the nature of the dienes. Cyclic and open-chain dienes that contain a system of double bonds like **1a**, **1c**, and **1d** underwent this reaction giving good yields of tetrahydrofuran or of tetrahydropyran-type cyclic ethers. On the other hand, **1e**, with its remote double bonds gave a low yield of the corresponding oxepane derivative as could be expected (only 3% at ambient temperature and 12% under reflux). However, **1b**, containing the same system of double bonds as **1c**, gave also a lower yield of ethers. We think that this is mainly caused by the conformational situation of the substrate as well as of the reaction products.



Isolated yields based on diphenyl diselenide; [a] at ambient temperature; [b] under reflux

Scheme 2

In our opinion, the reaction described above could be of interest for the synthesis of cyclic ethers or complex molecules containing these structural fragments. Its advantages are relatively cheap substrates, the simple experimental technique (which does not require expensive and complex equipment), and the ease of removal the phenylseleno group, either by oxidative or reductive methods [8].

Experimental

All chemicals, substrates, and electrode materials used were commercially available and were used as received. IR measurements were carried out with a Perkin-Elmer instrument (Model 137B). NMR spectra were obtained with a Varian Gemini (model 200) spectrometer (200 MHz) using *TMS* as internal standard and $CDCl_3$ as the solvent. As a direct current source, a Uniwatt, Beha Labor-Netzgerät (NG 394) was used. A cylindrical glass vessel supplied with a magnetic stirrer, electrodes (two 1.5×2.5 cm platinum foils), and a reflux condenser was used as an undivided cell for electrolysis.

In a typical procedure, 20 ml of an acetic acid/water (10:1) solution of 5 mmol of the corresponding substrate, 5 mmol of diphenyl diselenide, and 200 mg of $(C_2H_5)_4NCl$ were placed in the cell and electrolyzed at ambient temperature or under reflux. After passing 4 F/mol of electricity (200 mA, 32 min) through the mixture, electrolysis was stopped, and the resulting reaction mixture was stirred for 3 h, poured into 30 ml of water, and extracted with ether (3×30 ml). The organic layers were washed with a saturated solution of $NaHCO_3$, water, and brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residual oil was purified by column chromatography (SiO_2; petroleum ether/ethyl acetate = 20:1). All products of reactions (**2a**, **3a**, **2b**, **3b**, **2c**, **3c**, **2d**, and **2e**) are known compounds; their IR, ^1H NMR, and ^{13}C NMR spectroscopic data were identical with those described in the literature [5–7].

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