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KINETICS AND MECHANISM OF THE REACTION  
OF PHENYLSELENENYL HALOGENIDES  
AND SOME UNSATURATED ALCOHOLS

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In 1973 biochemical role of selenium in mammals was established. It was found that it is part of the active site of the antioxidant enzyme glutathione peroxidase (GPx). During the next decade came the explosive growth in the use of organo-selenium compounds. Very soon it was found that the phenylselenenyl groups are very good electrophilic reagents in organic synthesis, and in reactions with olefinic bonds they very often produce regio- and stereoselective products.

In past years we were performing intramolecular cyclization of some alkenols using PhSeX (X = Cl, Br). Obtained products (phenylseleno-ethers) could be easily manipulated and converted into many products with interesting biological properties like polyether antibiotics: monesin, narasin and tetronomycin. These reactions were performing under very mild conditions and removal (if necessary) of phenylseleno group can be easily done with oxidative or reductive methods. Intramolecular heterocyclization is the main reaction, between  $\Delta^4$  and  $\Delta^5$  primary alkenols and PhSeX, resulting the in formation of a tetrahydropyran and/or tetrahydrofuran type of rings.

In this research we observed kinetics and mechanism of 4-pent-1-ol, 5-heks-1-ol, E-4-heks-1-ol and Z-4-heks-1-ol with PhSeX in the presence and absence of pyridine in tetrachloromethane media. All reactions were studied as pseudo-first order reactions where the concentration of alcohol was always at least in 10-fold excess than the concentration of halogenide. The kinetics were followed by variable-temperature UV-VIS spectrophotometry and the changes of absorbance at suitable wavelength as a function of time were measured. The working wavelength for each substitution process was determined by preliminary repetitive scans in the range between 200 and 600 nm.

The reactions of phenylselenenyl halides and unsaturated alcohols are usually considered to be a two-step mechanism: electrophilic addition of the reagent to the double bond of the alkenols and nucleophilic attack of the hydroxylic oxygen results in the formation of a ring. This research have shown that reactions in presence of pyridine are faster then in its absence. Also reactions are faster with using PhSeCl then PhSeBr. The negative values of entropies of activation support an associative mechanism A or  $SN_2$ .