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Kinetic and Mechanistic Studies of Base-Catalyzed Phenylselenoetherification of *Z*- and *E*-hex-4-en-1-ols

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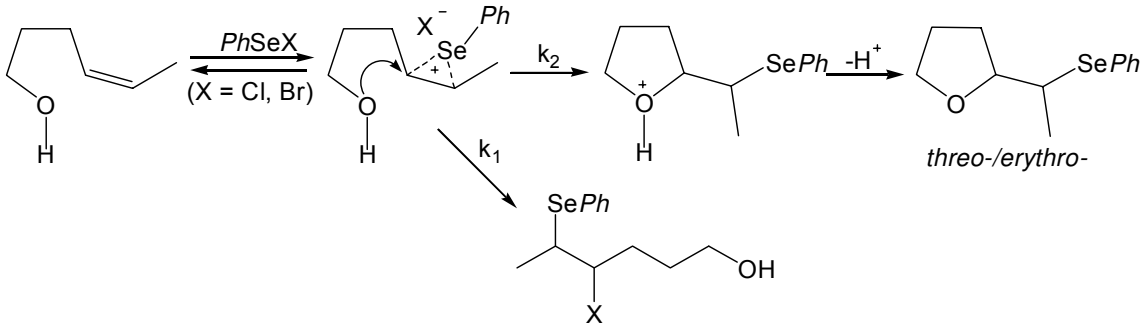
Organo-selenium induced cyclization of the unsaturated alcohols has been widely explored in organic synthesis over the last decade and depending on the nature of the substrate, a variety of five- and six-membered ring heterocycles can be prepared.[1,2] It must be emphasized that different regio- and stereoisomers can be produced in some cases by simply choosing conditions favorable to kinetic or thermodynamic control.[3]

In this work we reported a kinetic study of cyclization of two Δ^4-geometric isomers *Z*- and *E*-hex-4-en-1-ols with PhSeX (X=Cl, Br). From previous investigation, it is determined that (*E*)-isomer affords six-membered cyclic ethers as a unique product, while (*Z*)-isomer affords only five-membered cyclic ethers.[3] We investigated the influence of some Lewis bases (triethylamine, pyridine, quinoline, 2, 2'-bipyridne) on rate constants of the cyclization under the *pseudo*-first order conditions, in the presence and absence of bases, by UV-VIS spectrophotometry. Reactions were carried out in CCl_4 and THF as solvents. Values for rate constants are in according with pKa value of bases i.e. the fastest one is with triethylamine. The obtained values for rate constants have shown that the reactions with phenylselenenyl bromide are slower then with chloride. Cyclization reactions in THF as a solvent are faster then in non-polar CCl_4. Formations of tetrahydrofurane type of rings are faster reactions then formation of tetrahydropyrane type of rings. The negative values of entropies of activation support an assoaciative mechanism A or S_N2.



Literature:
[1] N. Petragnani et al., *Tetrahedron*, **2001**, *57*, 1411-1448. [2] M. Tiecco, et al. *Phosphorus, Sulfur and Silicon and the Related Elements,* **2005**, *180*, 729-740. [3] V. Divac, Z. Bugarcic, *Synthesis*, **2009**, *21*, 3684-3688.