REGIO- AND STEREOSELECTIVITY IN PHENYLSELENOETERYFICATION OF *Z*- AND *E*- HEX-4-EN-1-OLS

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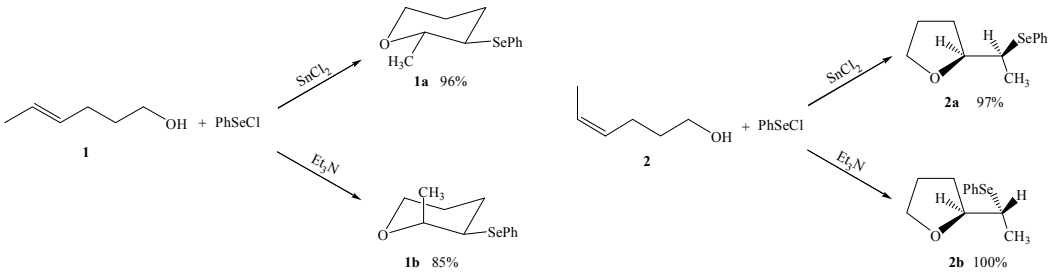
In 1973 biochemical role of selenium in mammals was established. It was found that it is a part of the active site of the antioxidant enzyme glutathione peroxidase (GPx)[1]. During the next decade came the explosive growth in the use of organoselenium compounds. Very soon it was found that the phenylselenenyl groups are very good electrophilic reagents in organic synthesis, and in reactions with olefin bonds they very often produce regio- and stereoselective products. In the presence of internal nucleophile (like in alkenols) the cyclization occurred.[2] Obtained products (phenylseleno-ethers) could be easily manipulated and converted into many products with interesting biological properties like, polyether antibiotics: monesin, narasin and tetronomycin[3]. Also some cyclic ethers are constituents of some molecules responsible for transport of the metallic cations Na^+, K^+, and Ca^{2+} through the lipid membranes[3], and as growth regulators[3,4] or inhibitors of the level of cholesterol in blood[5], etc. These reactions were performing under very mild conditions. The removal (if necessary) of phenylseleno group can be easily done with oxidative or reductive methods[6].

Intramolecular heterocyclization is the main reaction, between Δ^4 and Δ^5 primary alkenols and PhSeX, resulting in the formation of a tetrahydropyrane and/or tetrahydrofurane type of rings. In this work we succeeded to completely control stereo- and regio- selectivity in heterocyclization of Z and E hex-4-en-1-ols with usage of adequate additives. Alkenol 1 in presence of Et_3N as adtittive gives in excess cis- isomer (1b), and alkenol 2, erythro-isomer (2b). On the other hand presence of $SnCl_2$ with alkenol 1 forms only trans- isomer (1a), and threo- isomer (2a) with alkenol 2. The role of $SnCl_2$, as a weak Lewis-acid, is to collect halide ions from reagent, and so prevent concurrent attack of halide ion on selenonium cation intermediate. Stronger Lewis-acids would attack double bond itself and form the mixture of products. Et_3N as a base forms a hydrogen bond with proton from hydroxyl group and increases nucleophilyty of oxygen. Together bonded, hydroxyl group and Et_3N, make the steric disturbance so the attack of hydroxyl group is performed from the opposite side then expected. These additives not only provide selectivity, they also increase the yields to almost quantitative.



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