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2-P26. Kinetic studies for the phenylselenoetherification of 6-methyl-hept-5-en-2-ol in the presence of some additives

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Cyclic ether units are important synthetic targets in organic and medical chemistry due to their widespread occurrence in many complex natural compounds exhibiting important biological activities [1]. A number of synthetic approaches have been devised in order to construct the cyclic ether moiety. For some time we have been involved in the development and exploration of new methods for cyclofunctionalization of unsaturated alcohols.

For many reasons selenocyclofunctionalization has the advantage because the introduction of the heteroatom, the manipulation of the obtained product and the removal of the function are facilitated by simple and mild condition required [1]. This methodology has been extended to more complex systems having alcohol and double bond functions. In resent years we were investigating reactions between Δ^4- and Δ^5- unsaturated alcohols and phenylselenenyl halides PhSeX (X=Cl, Br) [2]. Intramolecular heterocyclization is the main reaction in the case of all investigated primary and secondary alkenols, but tertiary alkenols cyclized in good yields only in the presence of some additive. In the presence of additives such as pyridine, triethylamine, quinoline and 2,2′-bipyridine, yields of obtained cyclic ether products are increased to almost quantitative amounts in the case of all investigated alkenols. This observation may be ascribed to the role of the additives. It appears that the presence of some additives is beneficial to the cyclization process and more likely due to its basic properties. In addition, bases could enhance the nucleophilicity of the hydroxyl group of the alkenol and also mediate the stabilization of oxonium ion intermediate by abstracting the hydrogen. Prompted by what we found, we considered it synthetically interesting and profitable for our purposes to do some kinetic measurements to confirm that observation. We have used a conventional kinetic method to determine the values of rate constants and other thermodynamic parameters.

In this work we presented results of kinetic studies obtained by UV-vis spectrophotometry. We observed the reactions between 6-methyl-hept-5-en-2-ol and PhSeCl in the presence of following additives: pyridine, quinoline, 2,2′-bipyridine and triethylamine. All kinetic measurements were performed under pseudo first-order conditions, where [alkenol] was always ≥ 10-fold in excess over [PhSeCl] and [additives] in THF medium at a constant temperature of 15±0.1°C. There is a good agreement between the obtained values for rate constants and constants of additive's basicity. Therefore, the fastest reaction is the one with the additive which is the strongest base.

References

1. M. Tiecco, Top. Curr. Chem. 208 (2000) 7.
2. (a) B. Mojsilovic, Z. Bugarcic, Heteroatom Chem. 12 (2001) 475,393; (b) Z. M. Bugarčić, M. P. Gavrilović, V. M. Divac, Monats. Chem. 138 (2007) 149; (c) Z. Bugarcic, B. Mojsilovic, V. Divac, J. Mol. Catal. A Chem. 272 (2007) 288.