**Studies on the rearrangement of vinyl ethers and alkoxydienes in the synthesis of 4-, 5-, and 6-membered carbocyclic compounds**

Methodologies for the construction of new carbon-carbon bonds are fundamental reactions in organic synthesis. Especially valuable are reactions proceeding in a highly regio- and stereoselective manner, under mild reaction conditions.

There are many strategies that meet the above requirements, but of special importance are the rearrangement reactions. One of these is the Claisen rearrangement which allows the transformation of a variety of molecules into complex carbonyl compounds by using the [3,3]-sigmatropic rearrangement. It is one of the particular transformations of allyl vinyl and allyl aryl ethers leading to γ,δ-unsaturated carbonyl compounds. On the other hand, vinyl ethers undergo the less well-known, but also powerful in the terms of building complexity, [1,3]-rearrangement reaction. The Lewis acid-promoted [1,3] O-to-C rearrangement of vinyl ethers and acetals is believed, in general, to proceed via ionic cleavage, forming an ion pair (an enolate and a carbocationic species), followed by the recombination of the nascent stabilized carbocation with the enolate anion equivalent, generating a new carbon-carbon bond. The reaction strongly depends on the substrate structure and process conditions. The pioneering investigations made by Ferrier and Petasis showed that the vinyl ether [1,3]-rearrangement reaction is a useful tool in the synthesis of spatially defined natural products and biologically active compounds. The growing interest, promising results and applicability of this method have prompted the author to work on the modifications and evaluation of the presented methodology. It has been shown that certain alkoxydienes amenable to the creation of well-stabilized carbocations undergo the rearrangement reaction in a vinylogous manner with a substoichiometric amount of titanium chloride (IV). This rearrangement reaction proceeds with good chemical yield and regioselectivity to afford the corresponding cyclohexene carbaldehydes which are important structural synthons for the synthesis of numerous biologically active molecule.

The aim of this proposal, which is a creative continuation of works performed in the IChO PAS II group, is to develop a new, original, and reproducible method for the synthesis of highly substituted carbocyclic compounds (4-, 5-, and 6-membered), inaccessible by other methods. As a tool for the synthesis of the title compounds, the regioselective Lewis acid-catalyzed rearrangement of vinyl ethers and alkoxydienes will be utilized.

In the first step of our research the rearrangement reaction of five- and seven-membered cyclic dienes will be examined. These studies will allow to determine the scope of the developed method and allow to obtain functionalized carbocyclic compounds, ready for further modifications. Such compounds are difficult to synthesize by others methods, leaving a necessity to evolve new strategies. Next, the diastereoselective variant of the cyclic alkoxydiene rearrangement (vinylogous Ferrier-Petasis-type reaction) will be investigated.

The second objective of our proposal is the expansion of our methodology to the synthesis of valuable compounds such as substituted cyclobutanes, whose synthesis by other methods is a nontrivial task. Many derivatives containing the cyclobutane ring are not only valuable medicines, such as anti-diabetics or β-secretase inhibitors, but also synthetically useful molecules for the synthesis of 1,1'-spirobiindane scaffolds or eight-membered rings.

In the current proposal, the author would like to concentrate also on the stereoselective synthesis of cyclopentanes**.** The proposed method will allow to prepare not only simple cyclopentanes, but also enable the access to structurally more complex polyhydroxylated derivatives. Functionalized cyclopentanes are valuable synthetic targets, whose structure is present in a vast array of bioactive molecules. This core can be found in alkaloids, steroids, prostaglandins, triquinanes, indanes, guaianes, and many others. Although transformations leading to functionalized cyclopentane units are widely known, they are normally based on cycloaddition reactions or the direct transformation of commercially available substrates. The direct transformation of the carbocyclic compounds via the ring contraction seems to be a very attractive and convenient method for the synthesis of such derivatives. A marked advantage of this strategy is the fact that the reorganization of the bonds usually occurs with a high level of selectivity. Moreover, in many cases this transformation leads to structures not easily accessed by other methodologies.

In conclusion, the author proposes an innovative approach towards the stereoselective synthesis of structurally diverse, highly functionalized carbocyclic compounds. The implementation of the presented tasks will significantly enhance the sum of knowledge of the rearrangement reaction of the vinyl ethers, alkoxydienes, and related compounds, and will show that the developed transformation is a useful and unique strategy for the synthesis of structurally complex molecules difficult to synthesize by other methods.