

DFT study of the mechanism of the phenylselenoetherification reaction of linalool

Nenad Janković, Svetlana Marković & Zorica Bugarčić

Monatshefte für Chemie - Chemical Monthly

An International Journal of Chemistry

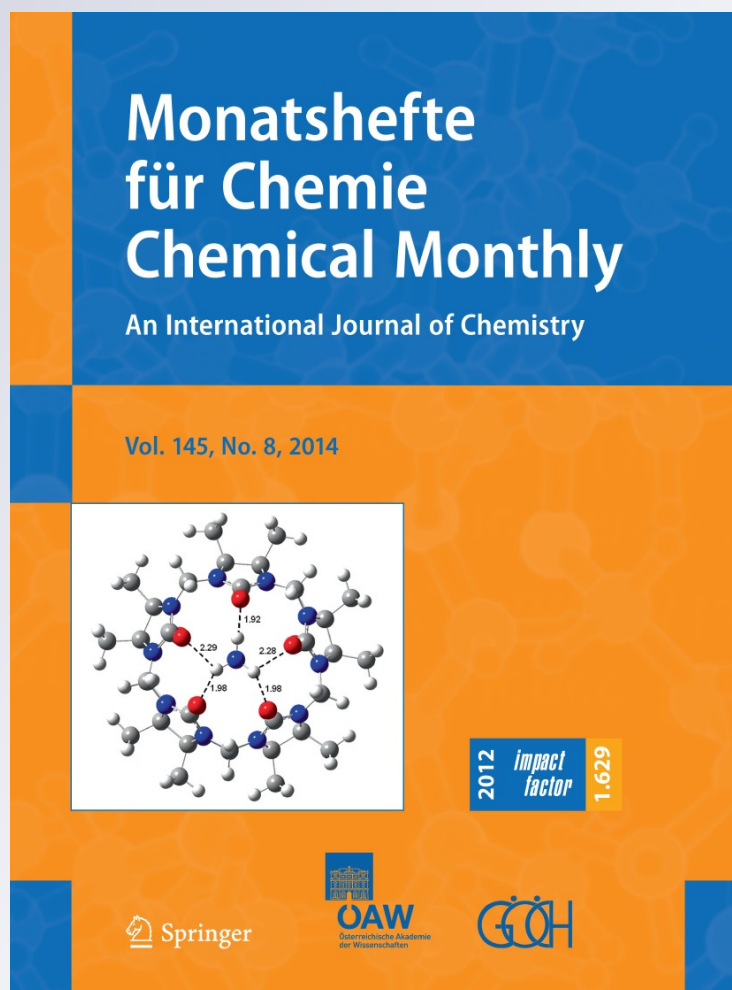
ISSN 0026-9247

Volume 145

Number 8

Monatsh Chem (2014) 145:1287-1296

DOI 10.1007/s00706-014-1226-5



Your article is protected by copyright and all rights are held exclusively by Springer-Verlag Wien. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".

DFT study of the mechanism of the phenylselenoetherification reaction of linalool

Nenad Janković · Svetlana Marković ·
Zorica Bugarčić

Received: 25 December 2013 / Accepted: 6 April 2014 / Published online: 24 May 2014
© Springer-Verlag Wien 2014

Abstract A systematic study of the mechanism of phenylselenoetherification of a naturally occurring alcohol linalool with PhSe^+ was performed at the B3LYP/6-311+G(d,p) level of theory, in conjunction with the CPCM solvation model. The *syn* and *anti* reaction pathways were examined in the absence and presence of some Lewis bases (quinoline, piperidine, pyridine, and triethylamine) as catalysts. It was found that the reaction occurs via the phenylseleniranium intermediate, which further suffers a nucleophilic attack of the oxygen to two olefinic carbon atoms. This intramolecular cyclization yields 5-ethenyl-5-methyl-2-[2-(phenylseleno)-prop-2-yl]tetrahydrofuran as the major product and 6-ethenyl-2,2,6-trimethyl-3-phenylselenotetrahydropyran as the minor product. Lewis bases facilitate the reaction by strong hydrogen bonds between the alcoholic hydrogen and nitrogen of an additive moiety, and they stabilize the product complexes. Since the formation of the tetrahydrofuran derivative requires higher activation energy, but is thermodynamically more stable than the tetrahydropyran, it was concluded that the phenylselenoetherification reaction of linalool is thermodynamically controlled.

Keywords Alcohol · Cyclization · Reaction mechanism · Catalyst

Introduction

Substituted tetrahydrofuran and tetrahydropyran rings are common in many natural products and play an important role as building blocks for the synthesis of various biologically active organic target molecules [1]. Stereoselective synthesis of substituted cyclic ethers [2, 3] is important and requires considerable attention since cyclic ether units are frequently found in polyether antibiotics [4–6], C-glycosides [7–10], and polyene mycotoxins [11–15].

Cyclization of unsaturated alcohols leading to cyclic ethers is well documented in the literature as a convenient pathway in the synthesis of natural products and related compounds [16]. Different electrophilic selenium reagents and a variety of reaction conditions have been employed, and recent reviews highlight the broad scope of this general procedure [17–20]. In recent years, we have studied intramolecular cyclizations of some Δ^4 - and Δ^5 -alkenols by means of phenylselenenyl halides [21–29]. The outcome of these reactions is influenced by the nature of the selenium reagent used. The use of phenylselenenyl halides in these reactions can lead to some side reactions, such as the addition of PhSeX to the double bond of the alkenol.

Although procedures for these cyclizations have been well established, the interactions between the selenium electrophile, counterion, solvent, and substrate have not been fully understood. In a recent article [29], density functional theory was used to simulate phenylselenoetherification of pent-4-en-1-ol. It was shown that the cyclization occurs via an $\text{S}_{\text{N}}2$ -like transition state, leading to the generation of a THF-type phenylseleno ether. When an additive is not present in the reaction system, the process is endothermic, whereas in the presence of pyridine the reaction is exothermic. In addition, quantum-chemical

Electronic supplementary material The online version of this article (doi:10.1007/s00706-014-1226-5) contains supplementary material, which is available to authorized users.

N. Janković · S. Marković (✉) · Z. Bugarčić
Department of Chemistry, Faculty of Science, University of
Kragujevac, Radoja Domanovića 12, P.O. Box 60,
34 000 Kragujevac, Serbia
e-mail: mark@kg.ac.rs

