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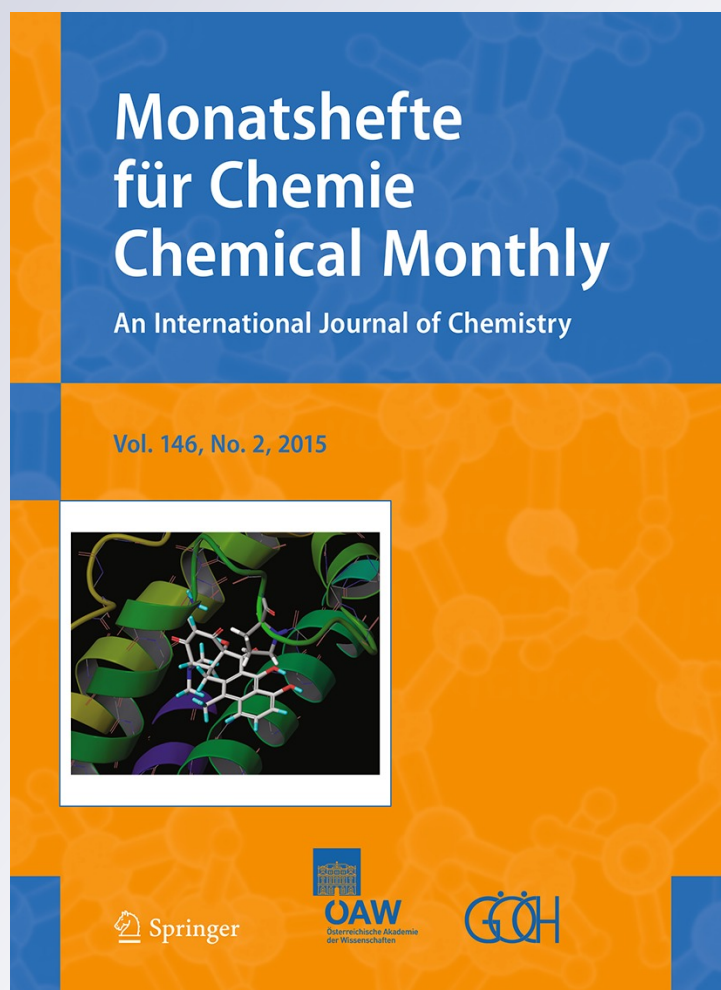
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Influence of the counteranion on the phenylselenoetherification reaction of nerolidol

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Abstract The pyridine-mediated reactions of nerolidol with both PhSe^+ and PhSeCl were investigated using two DFT methods. Comparison of the obtained results provides a description of the counterion influence for the first time. As a consequence of very low solvation free energy of the neutral reactants, addition of the phenylselenyl group to the double bond of nerolidol is an endergonic process, and occurs via a transition state to yield an intermediate that undergoes cyclisation. Due to the influence of the counteranion on the positively charged moiety of the reaction system, the activation free energies in the reaction with PhSeCl are significantly larger than those in the reaction with PhSe^+ . Thus, only the *anti* pathway is favoured. The lower activation energy required for the formation of less stable *cis*-5-ethenyl-5-methyl-2-[6-methyl-2-(phenylseleno)hept-5-en-2-yl]tetrahydrofuran confirms that the examined reaction is kinetically controlled.

Keywords Alcohol · Cyclisation · Reaction mechanism · Catalyst

Introduction

The substituted tetrahydrofuran (THF) rings are structural fragments found in numerous biologically active, naturally

occurring molecules such as polyether antibiotics [1, 2], C-glycosides [3–6], and polyene mycotoxins [7, 8]. A number of different synthetic methods have been developed to construct this ring. Some synthetic strategies include carbonyl ylide dipolar cycloaddition [9], Prins pinacol reaction [10], and Oshima-Utimoto reaction [11, 12]. Also, tetrahydrofuran ring can be constructed via a catalysed inter- [13] or intramolecular [14–17] cyclisation. Very important reaction for the THF ring construction is cyclofunctionalization of unsaturated alcohols. Some alkenols can be found in nature in the form of essential oils which showed different biological activities [18–22]. One of the components of the essential oils is a natural sesquiterpene nerolidol, also known as peruvicol.

Phenylselenoetherification is a reaction for the production of cyclic ethers with tetrahydrofuran and tetrahydropyran rings, which has been attracting attention of our research group for more than a decade [23–33]. Although phenylselenoetherification of unsaturated alcohols has been the subject of some theoretical investigations [29, 30, 33], the reaction mechanism has not been fully elucidated. It was revealed that the cyclisations of pent-4-en-1-ol [29], (Z)-hex-4-en-1-ol, (E)-hex-4-en-1-ol [30], and linalool [33] take place via the $\text{S}_{\text{N}}2$ -like transition states. The reaction major products are the THF-type phenylseleno ethers, whereas the ethers containing the tetrahydropyranoid ring are formed at negligible amounts. It was demonstrated that Lewis bases lower activation energies and stabilise reaction products [29, 33]. It was concluded, by using an ammonia molecule to estimate the influence of different additives to the cyclisation of (Z)-hex-4-en-1-ol, that the reaction is kinetically controlled [30]. The mechanism of phenylselenoetherification of linalool was systematically studied, implying that all *syn* and *anti* routes, catalysed with quinoline, piperidine, pyridine,

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