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ORIGINAL RESEARCH

Kinetic and mechanistic insight into Lewis base and acid-mediated phenylselenoetherification of 2,6-dimethyl-hept-5-en-2-ol

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Abstract Mechanistic and kinetic aspects, as well as quantum chemical calculations, for the formation of a tetrahydrofurane ring by cyclization of the highly substituted alcohol–2,6-dimethyl-hept-5-en-2-ol with phenylselenohalides (PhSeCl and PhSeBr), in the presence of various Lewis bases (piperidine, triethylamine, pyridine and quinoline) and Lewis acids ($CoCl_2$, $SnCl_2$) as additives were studied. The substituted tetrahydrofuran ring is common motif in many natural products, especially in bioactive marine macrolides. Due to the presence of additives in reactions, the high regioselectivity was achieved, and the tetrahydrofuran type of ether in all studied reactions was obtained in excess in regard to the six-membered cyclic ether. In addition, kinetic aspects of reactions mediated by Lewis bases were studied by UV–Vis spectroscopy (in THF, at 288 K), as reactions of *pseudo*-first-order. Obtained values for rate constants proved catalytic role of additives and indicated that the reaction rate depends on pKa values of used base as well as on their ability for formation of hydrogen bond with OH–alcohols group.

Keywords Kinetics · Cyclization · Transition state structure · Quantum calculations

Introduction

Substituted oxygen heterocycles, particularly five- and six-membered cyclic ethers, have attracted special attention in recent years due to their occurrence as structural units of many bioactive natural products, such as polyether antibiotics, acetogenins and C-glycosides [1–4]. Thus, the development of methods that enable access to their effective construction is of significant importance, and many strategies have been explored for this purpose [5–9]. It is now well established that selenium-induced cyclofunctionalization of unsaturated alcohols represents an easy access to a wide variety of heterocyclic compounds containing oxygen atom [10, 11]. This synthetic method has the advantage that the introduction of the heteroatom, the manipulation of the obtained product and the removal of the function from the side chain is facilitated by simple and mild experimental conditions.

As a part of our ongoing research, directed toward the intramolecular cyclization of unsaturated alcohols by means of phenylselenenyl halides as reagents, we have examined the chemo-, regio-, stereoselectivity and reaction kinetics as a function of substitution pattern at the double bond and at the carbinol carbon atom of the used alkenol substrate. The influence of some Lewis acids and bases as catalysts on mechanistic pathway and reaction rate has also been evaluated [12–21].

Electronic supplementary material The online version of this article (doi:10.1007/s11224-015-0570-3) contains supplementary material, which is available to authorized users.

In memoriam to Prof. Dr. Dr. *h.c. mult.* Paul von Ragué Schleyer (February 27 1930–November 21 2014) sc

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The present paper deals with synthetic, mechanistic and kinetic aspects of the reaction between the tertiary alkenol (2,6-dimethyl-hept-5-en-2-ol) which has a highly substituted double bond and the phenylselenyl halides (PhSeBr and PhSeCl), in the presence of some Lewis bases and acids as additives (piperidine, pyridine, quinoline, triethylamin, $CoCl_2$ and $SnCl_2$).

Result and discussion

Cyclofunctionalization of Δ^4- and Δ^5-unsaturated alkenols, by means of PhSeX (X = Cl, Br) as reagents, occurs through the formation of a seleniranium ion and the subsequent attack of the OH group. Depending on the reaction conditions, the formation of seleniranium ion can be reversible process and at low temperatures usually under kinetic control [10, 22]. While the selenocyclofunctionalization of primary and secondary alkenols is usually driven by electronic factors, and formation of corresponding five- or six- membered rings occurs in Markovnikov fashion (regioselectivity), the effect of steric hindrances is decisive in the course of tertiary alkenol transformation, where the product of anti-Markovnikov's rule can be expected. Substituents at the carbinol carbon atom display strong influence on the decrease in yields of cyclic ether products. Therefore, transformation of primary alkenols proceeds in moderate to good yields, secondary alkenols cyclizate in considerable lower extent, while tertiary alkenols do not undergo cyclization with PhSeBr, and in small yields with PhSeCl as a reagent.

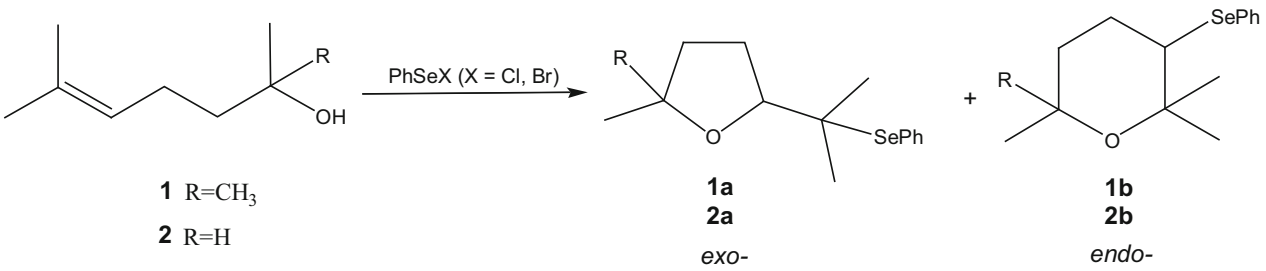
Cyclofunctionalization of 2,6-dimethyl-hept-5-en-2-ol **1** with PhSeX (X = Cl, Br) can afford two structural isomers (substituted tetrahydrofuran **1a** or tetrahydropyran **1b** type of cyclic ethers), through *exo*- and *endo*-cyclization pathway (Scheme 1). A previous study has shown that its secondary analog (6-methyl-hept-5-en-2-ol **2**) at −78, 0 °C and room temperature gave only the six-membered cyclic ether **2b** as a result of Markovnikov's orientation, regardless of the employed cyclization reagent. An increase of only one methyl group at the carbinol carbon atom in our substrate **1**, in regard to its secondary analog, leads to the steric control of the reaction and predominantly formation of five-membered ring **1a** by *exo*-cyclization pathway at −78 and 0 °C, while at room temperature, the six-membered ring **1b** was obtained as main reaction product (Scheme 1) [23]. This is another validation of the very delicate relationship between electronic and steric contributions on the final outcome of the reaction. No cyclization products were observed in the case of **1** when the PhSeBr was used as reagent.

Scheme 2 describes the mechanism of the phenylselenoetherification of 2,6-dimethyl-hept-5-en-2-ol as a two-stepped process. The first phase of the reaction involves the electrophilic attack of the phenylselenenyl group on the double bond of the alkenol, which results in the formation of a seleniranium ion **I**. In the next phase of the reaction, the nucleophilic attack of the hydroxyl oxygen occurs, which result in the formation of the oxonium ions **Ia** and **Ib**. Finally, the formation of the five- and six-membered cyclic ethers, **1a** and/or **1b**, occurs with the elimination of the protons from the oxonium ions. The presence of the nucleophilic halide anion is sometimes responsible for some undesirable processes such as its attack on the selenonium ion and the formation of the side product **1c**, which causes a lower yield of the cyclic ether products.

In order to decrease the side reactions and to increase the yields of cyclic products, we performed experiments with two different sets of additives: some Lewis acids ($SnCl_2$, $CoCl_2$) and some Lewis bases/Brønsted bases (piperidine, triethylamine, pyridine and quinoline). The obtained results are presented in Table 1. The use of equimolar amounts of Lewis/Brønsted bases and acids as additives led to almost quantitative yields of the cyclic ethers, even in the case of PhSeBr as the reagent. The distribution of products proceeds with higher regioselectivity than in the case of reactions without present additive. In all investigated reactions, tetrahydrofuran type of ether was obtained in excess. The best results in terms of regioselectivity were achieved with $SnCl_2$ as the catalyst. The role of Lewis acids in these reactions is to increase the electrophilicity of the reagent (PhSeX) and to decrease a possibility of halide addition by removing the anion from the reagent and in that way to improve the yields of the desired cyclic products.

The merit for the increased yields in the reactions with bases can be ascribed to the ability of the Brønsted bases to form hydrogen bonds with the substrate's OH group, facilitating the formation of the cyclic ether. The rapid abstraction of a proton stabilizes the intermediate directs its transformation to the product [18]. Since there are increased steric demands for the OH nucleophilic approach due to hydrogen bonded base, the formation of the main reaction product is determined by the OH attack on the sterically less hindered C-5 carbon as shown in Fig. 1 (anti-Markovnikov orientation).

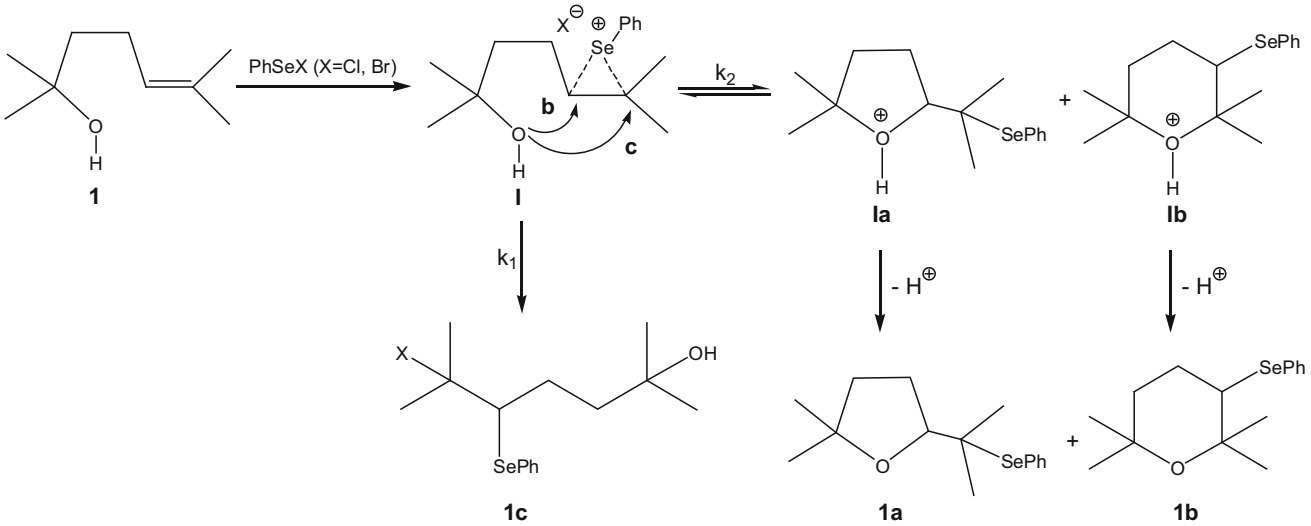
To get an impression of the influence of the steric effects of the applied base in comparison with the consequences of CH_3 groups neighboring to the two reactive motifs, the OH group and the double bond, we performed quantum chemical calculations. As we investigated the possible reaction pathways already before [18, 19], we focused here on a comparison of the transition states leading to the five- and six-membered ether applying the smallest possible base NH_3 as in our earlier studies [18, 19]. As alkenoles, we utilized of course 2,6-dimethyl-hept-5-en-2-ol and 6-methyl-hept-5-



Reagent	Substrate	-78 °C	0 °C	r.t
PhSeCl	**1**[a]	75 % (95:5)	45 % (66:34)	37 % (31:69)
	2[b]	90 % (0:100)	73 % (0:100)	68 % (0:100)
PhSeBr	**1**[a]	/	/	/
	2[b]	30 % (0:100)	22 %(0:100)	18 % (0:100)

a - ratio in parentheses 1a:1b; b - ratio in parentheses 2a:2b

Scheme 1 Selenocyclofunctionalization of 2,6-dimethyl-hept-5-en-2-ol and 6-methyl-hept-5-en-2-ol



Scheme 2 Mechanism of the phenylselenoetherification of 2,6-dimethyl-hept-5-en-2-ol

Table 1 Yields (%) and ratio (**1a:1b**) of cyclic ether products in the phenylselenoetherification of 2,6-dimethyl-hept-5-en-2-ol in the presence of some Lewis bases and acids as additives

	Without additive	Et_3N	Pyridine	Quinoline	Piperidine	$CoCl_2$	$SnCl_2$
PhSeCl	37	98	96	98	100	98	97
	(69:31)	(86:14)	(95:5)	(84:16)	(96:4)	(96:4)	(100:0)
PhSeBr	–	99	99	99	100	97	96
	–	(96:4)	(86:14)	(96:4)	(97:3)	(95:5)	(100:0)

en-2-ol to get an impression of the influence of an extra methyl group next to OH. For both alkenoles, the transition state leading to the furanoide ether is significantly more stable than the transition state leading to the pyranoide form, independently if we compare B3LYP or MP2(fc) energies (see Table 2; Figs. 2, 3) The extra methyl group in 2,6-

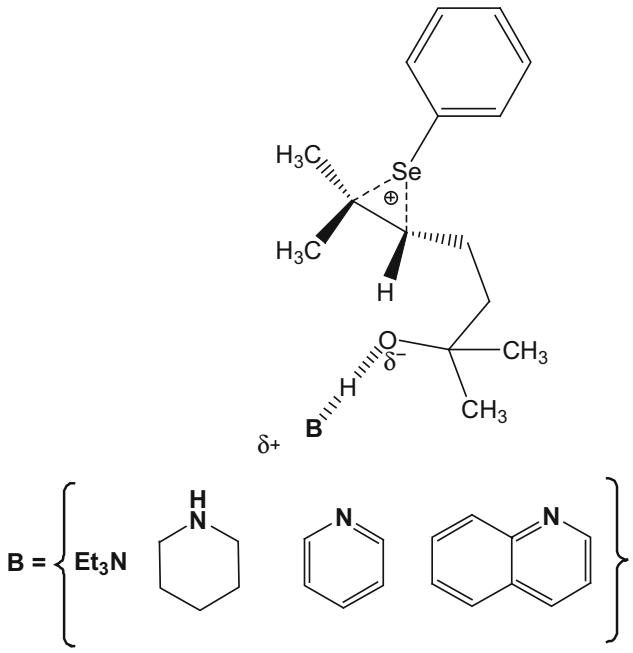


Fig. 1 Steric hindrance during the ring-closing phase in the reactions facilitated by bases

dimethyl-hept-5-en-2-ol shows, compared to 6-methyl-hept-5-en-2-ol, only an insignificant influence on the transition state's selectivity beyond the accuracy of the applied quantum chemical methods.

Therefore, we calculated the possible five- and six-membered cyclic phenylseleno ethers. In the case of the cyclic systems derived from 2,6-dimethyl-hept-5-en-2-ol, the resulting compound tetrahydro-2,2-dimethyl-5-(2-(phenylselanyl)propan-2-yl)furan and tetrahydro-2,2,6,6-tetramethyl-3-(phenylselanyl)-2H-pyran within the accuracy of the applied methods best addressed as energetic equal (pyranoid forms a bit less stable MP2: +1.3 kcal/mol B3LYP: 0,1 kcal/mol). This is clearly different in the case of 6-methyl-hept-5-en-2-ol, here tetrahydro-2,2,6-trimethyl-3-(phenylselanyl)-2H-pyran is around 5 kcal/mol more stable (MP2: 4.2 kcal/mol, B3LYP: 5.6 kcal/mol) than tetrahydro-2-methyl-5-(2-(phenylselanyl)propan-2-yl)furan.

In accordance with earlier findings [18, 19], the distance between the entering $H_3N\cdots HO$ group and the formally sp^2-C-atom, dedicated to form the new bond, in the furanoide transition states are consequently shorter (2,6-dimethyl-hept-5-en-2-ol: 2.08 Å, 6-methyl-hept-5-en-2-ol: 2.04 Å) than in the pyranoide's form transition state (2,6-dimethyl-hept-5-en-2-ol: 2.16 Å, 6-methyl-hept-5-en-2-ol: 2.14 Å).

In order to compare the impact of the used base additives on the reaction pathway and rate constants, conventional kinetic method by UV/Vis spectroscopy was used. All reactions were studied as reactions of *pseudo*-first-order at 288 K in THF as solvent. The attack on the selenonium cation by the OH internal nucleophile was considered as the rate determining step. Reactions were investigated by following the dependence of the absorbance on reaction time at suitable wavelength. The calculations for the k_{obsd} are explained in the "Experimental section" section and the data are given in Tables 1S and 2S (Supplementary material). The observed rate constants as a function of total alcohol concentration can be described by the following equation:

$$k_{obsd} = k_1 + k_2[\text{alcohol}]$$

In this equation, k_2 represents the second-order rate constant for the forward reaction (cyclization reaction), which depends on alcohol concentration, and k_1 shows the effects of the parallel reaction (reaction of addition). The rate constant k_1 is independent of the alcohol concentration. The values of k_2 were calculated from the slopes of the plots k_{obsd} versus the alcohol concentration, while the values for k_1 were determined from the intercept of the observed lines. (Table 3; Fig. 4) [24].

From the results given in Table 3, it can be seen that in the catalyzed reactions with PhSeCl as the reagent, the values for the rate constants are from 2 to 6 orders of magnitude higher than in the case of the uncatalyzed reactions. Furthermore, the variation of used cyclization reagent has significant influence on the reaction rate. The values of the rate constants for the catalyzed reactions with PhSeCl as the reagent are higher than for analogs reactions with PhSeBr. Additionally, it was found that the efficiency of the used catalysts is following the order: piperidine > triethylamine > pyridine > quinoline, which corresponds

Table 2 Calculated energy differences of the two possible transition states

	ts leading to the furanoide ether	ts leading to the pyranoide ether
2,6-dimethyl-hept-5-en-2-ol	0,0 kcal/mol (0,0 kcal/mol)	+5,9 kcal/mol (+3.9 kcal/mol)
6-methyl-hept-5-en-2-ol	0,0 kcal/mol (0,0 kcal/mol)	+6.1 kcal/mol (+3.7 kcal/mol)

MP2(fc)/6-311+G**//B3LYP/6-311+G** + ZPE(B3LYP/6-311+G**)

Values in parentheses: B3LYP/6-311+G** + ZPE(B3LYP/6-311+G**)

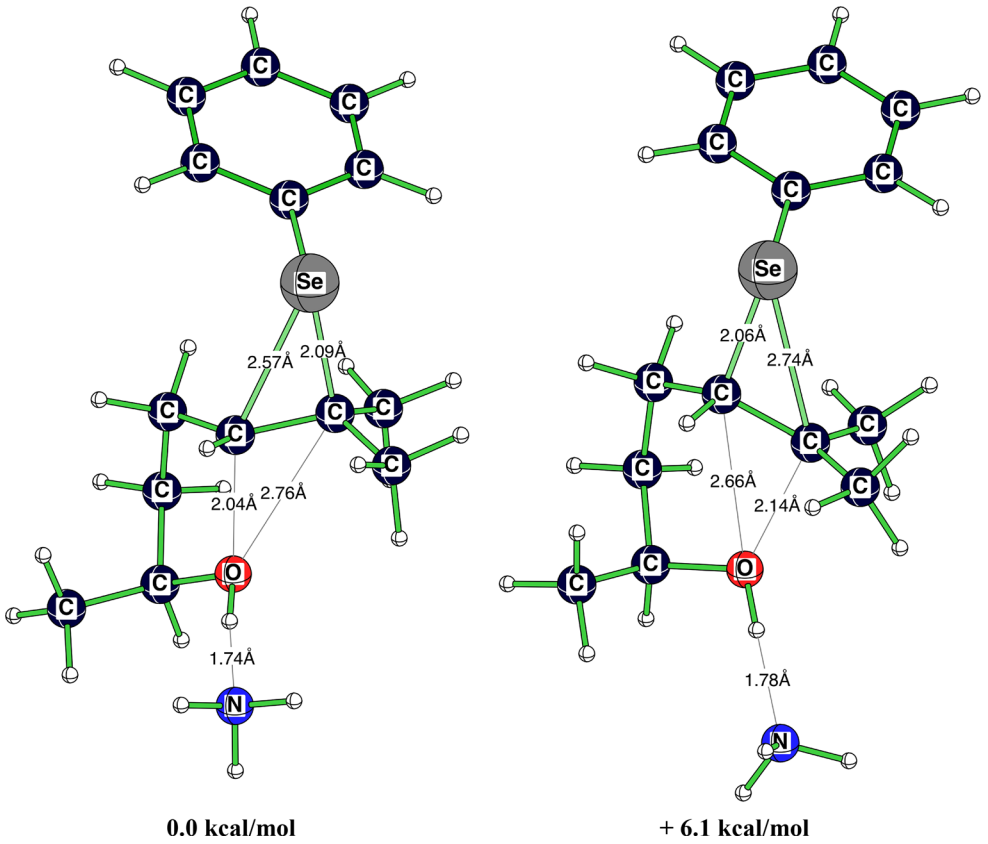


Fig. 2 Calculated transition states for furanoid and pyranoid form for phenylselenoetherification of 6-methyl-hept-5-en-2-ol

to the pKa values of the used bases [25, 26]. The results listed in Table 2 indicate that the nature of the used bases has a strong impact on their catalytic activity. It is well known that the ring-closing phase is highly sensitive on increase of the steric hindrances and therefore can often cause the change of the reaction pathway. Thus, despite the highest ability of triethylamine for hydrogen bond formation (DN = 61) the opposite to piperidine's (DN = 40), its catalytic activity is relatively shrunk due to its greater steric necessities.

From the graphs in Fig. 3, it can be seen that the plots of k_{obsd} versus [alcohol] are linear. All graphs of catalyzed reactions start from the origin, demonstrating the values for the constants k_1 are insignificantly small, which is in agreement with the preparative results (no parallel reaction present). In contrast, in the uncatalyzed reaction with PhSeCl, an intercept occurs (value for k_1 shown in Table 3). The plot of k_{obsd} versus [alcohol], with PhSeBr as a reagent, is not presented, because no cyclization products are observed under these experimental conditions (Table 1).

The linear relationship in the Brønsted plot of log k_2 versus pKa indicates that all used catalysts, despite their structural differences, increase the reaction rates if the same reaction mechanisms are traversed (Fig. 5).

Experimental section

General. Gas–liquid chromatography (GLC) analyses were performed with a Deni instrument, model 2000 with capillary apolar columns. ^{1}H and ^{13}C NMR spectra were run in $CDCl_3$ on a Varian Gemini 200 MHz NMR spectrometar. IR spectra were obtained with Perkin-Elmer Model 137B and Nicolet 7000 FT spectrophotometers. Thin-layer chromatography (TLC) was carried out on 0.25 mm E. Merck precoated silica gel plates (60F-254) using UV light for visualization. For column chromatography, E. Merck silica gel (60, particle size 0.063–0.200 mm) was used.

For the kinetic measurements, UV–Vis Perkin Elmer Lambda 35 spectrophotometer equipped with a thermostatted cell was used.

General synthetic procedure

All reactions were carried out on a 1 mmol scale. To a magnetically stirred solution of the alkenol (1 mmol) and the additive (1 mmol) in dry dichloromethane (5 cm^3), solid PhSeX (X = Cl or Br) (1.1 mmol) was added at room temperature. The reaction went to completion in a few minutes. The pale yellow solution was washed with 5 ml of 1 M HCl

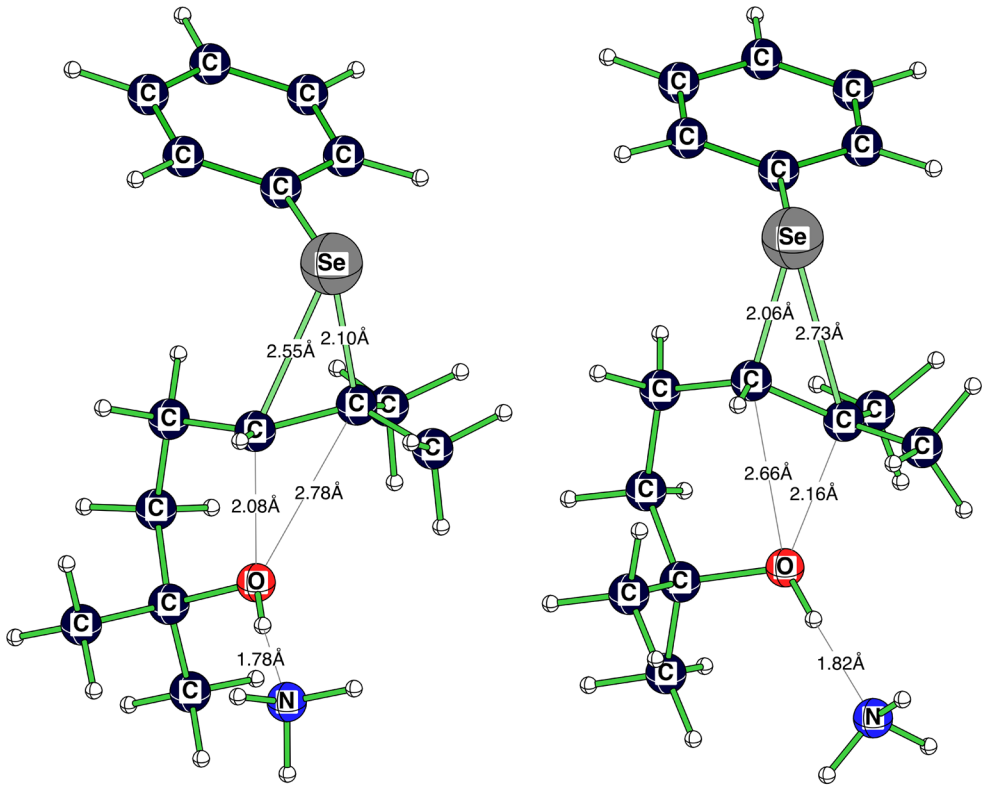


Fig. 3 Calculated transition states for furanoid and pyranoid form for phenylselenoetherification of 2,6-dimethyl-hept-5-en-2-ol

Table 3 Rate constants for phenylselenoetherification of 2,6-dimethyl-hept-5-en-2-ol in THF at 288 K

	PhSeCl			PhSeBr	
	pKa	k_2 ($M^{-1}s^{-1}$)	k_1 (s^{-1})	k_2 ($M^{-1}s^{-1}$)	k_1 (s^{-1})
Without catalyst	–	0.28 ± 0.02	(8 ± 9) × 10^{-5}	–**	–
Quinoline	4.92	0.46 ± 0.05	–*	0,3 ± 0,02	–
Pyridine	5.2	0.54 ± 0.04	–	0.38 ± 0.04	–
Triethylamine	10.78	1.08 ± 0.05	–	0.62 ± 0.06	–
Piperidine	11.2	1.7 ± 0.1	–	0.74 ± 0.02	–

* The values for k1 are insignificantly small and therefore not presented

** No cyclization products were observed in reaction with PhSeBr, without catalyst present

aqueous solution (only in case of Lewis bases as additives), then saturated $NaHCO_3$ aqueous solution and water. The organic layer was dried over Na_2SO_4, concentrated and chromatographed. The product was obtained after the elution of the traces of diphenyl diselenide from a silica gel-dichloromethane column. All products were characterized and identified on the basis of their spectral data [23].

Kinetic measurements

For determination of the rate constants, conventional kinetics was used. The temperature of reaction mixtures was controlled throughout all kinetic experiments to ±0.1 °C. Reactions were performed at 288 K. The solutions of reactants were prepared by measuring calculated amounts of substances in THF as a solvent. THF is more suitable than dichloromethane for kinetic experiments in terms of the boiling point, but for synthetic purpose, it is better to use dichloromethane which can be removed easily from reaction mixture. In a quartz cuvette, a certain volume of alcohol solution was added, then catalyst, and the reaction was initiated by adding phenylselenenyl halide. During all experiments, the concentration of phenylselenenyl halide was kept constant (1 × 10^{-4} M), while the concentration of

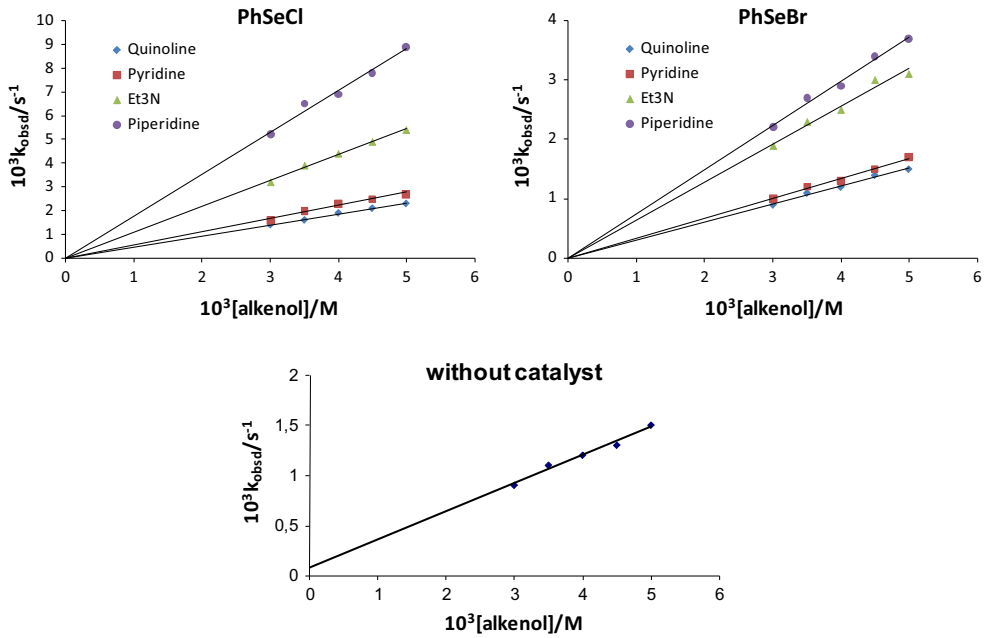


Fig. 4 *Pseudo*-first-order rate constant, k_{obsd}, as a function of the alkenol concentration for the reaction between 2,6-dimethyl-hept-5en-2-ol and PhSeX (X = Cl, Br), in the presence and absence of the catalysts

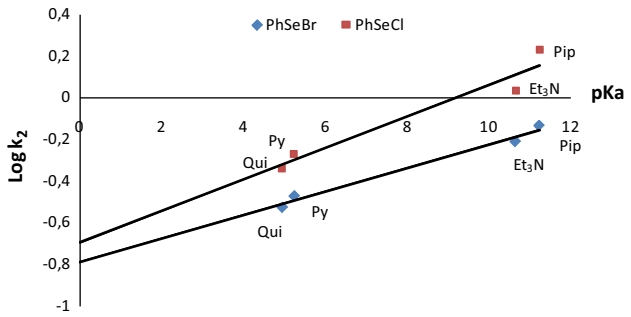


Fig. 5 Bronsted plot of log k_2 versus pKa for the catalyzed reaction between PhSeX and 2,6-dimethyl-hept-5-en-2-ol

alcohol was 5×10^{-3}, 4.5×10^{-3}, 4×10^{-3}, 3.5×10^{-3} and 3×10^{-3} M. In the reactions with catalyst present, concentrations of catalysts were equimolar to phenylselenenyl halide concentration. All reactions were investigated by following the dependence of the absorbance on reaction time at suitable wavelength. The *pseudo*-first-rate constants, k_{obsd}, were determined according to the equation by fitting all kinetic runs as single exponential function.

$$A_t = A_0 + (A_0 - A_\infty) \exp(-k_{obsd} t)$$

The observed *pseudo*-first-order rate constants were calculated as the average value from two to five-independent kinetic runs using Microsoft Excel and Origin 6.1. Obtained experimental data are reported in Tables 1S and 2S (Supplementary material).

Quantum chemical calculations

All structures were fully optimized at B3LYP/6-311+G** [27–30] and characterized as transition state structures by computation of vibrational frequencies (for transition state structures, exactly one imaginary frequency is present, NImag = 1). Being well aware of the limitations of DFT calculations, [31–35] we evaluated the energies by MP2(fc)/6-311+G** calculations [MP2(fc)/6-311+G**//B3LYP/6-311+G** + ZPE(B3LYP/6-311+G**)] [36]. Gaussian 03 suites of programs were used throughout [37].

Conclusions

Phenylselenoetherification of 2,6-dimethyl-hept-5-en-2-ol presents a way for the synthesis of the highly substituted cyclic ether products. These ether units are widespread in many bioactive natural products. The regioselective outcome of the reaction can be controlled by the proper choice of the Lewis base and acid catalyst. The reactivity of the used Lewis base catalyst depends on their pKa values as well as on their ability for formation of hydrogen bond with OH– alcohols group. In addition, quantum chemical calculation have confirmed the preferentially formation of the tetrahydrofuran ring. Being aware of these findings, the used methodology can be applied on the wide range of unsaturated substrates in order to increase the reaction

yield, decrease the reaction time and improve the reaction selectivity.

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