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Kinetic study of phenilselenoetherification of α-terpineol, cineol precursor

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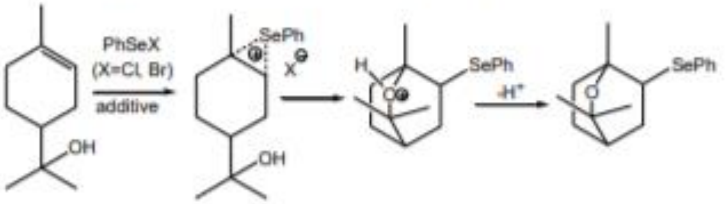
Cyclofunctionalizations of alkenols

Unsaturated alcohols, with convenient position of a double bond and a hydroxyl group, undergo intramolecular cyclization process, giving THF and THP ring type products. By using phenilselenohalides as reagents, these cyclizations occur very fast, under mild conditions, with the added benefit of easy PhSe-group removal, and also manifesting in high yields of cyclic products [1]. The importancy of cyclic ethers obtained in this way is shown in their vast presence in natural products and pharmaceutical compounds, as well as in their biological activity and synthetic value. Important natural product, cineol, can easily be obtained by phenylselenoetherification of α-terpineol [2]. In order to further improve this reaction, we felt necessary to examine the kinetics and mechanism under which the intramolecular cyclizacion occur.

As it can be seen from the Scheme, this is the two step mechanism, where the nucleophilic attack of pendant hydroxil group is a rate determing step.



α - terpineol

additive : Et_3N, Pipy, Py, Bipy, Qui

The mechanism of phenylselenoetherification of α-terpineol using PhSeCl and PhSeBr as reagents, some Lewis bases (triethylamine, pyridine, pipyridine, quinoline, 2,2′-bipyridine) as catalysts, in THF as a solvent was examined through kinetic study by UV–Vis spectrophotometry, under *pseudo*-first order conditions, where we determined rate constants for the cyclization reactions (k_2) and competitive, addition reaction (k_1). The obtained values for rate constants k_2 show that the reactions with PhSeBr are slower then those with PhSeCl. The reaction with piperidine is the fastest one. The presence of base catalyst supressess the competitive reaction almost completly ($k_1 \approx 0$). It is found that these reactions follow the mechanism of bimolecular nuclephile substitution S_N2 pathway, which is in accordance with our previous experimental findings [3].

References

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