



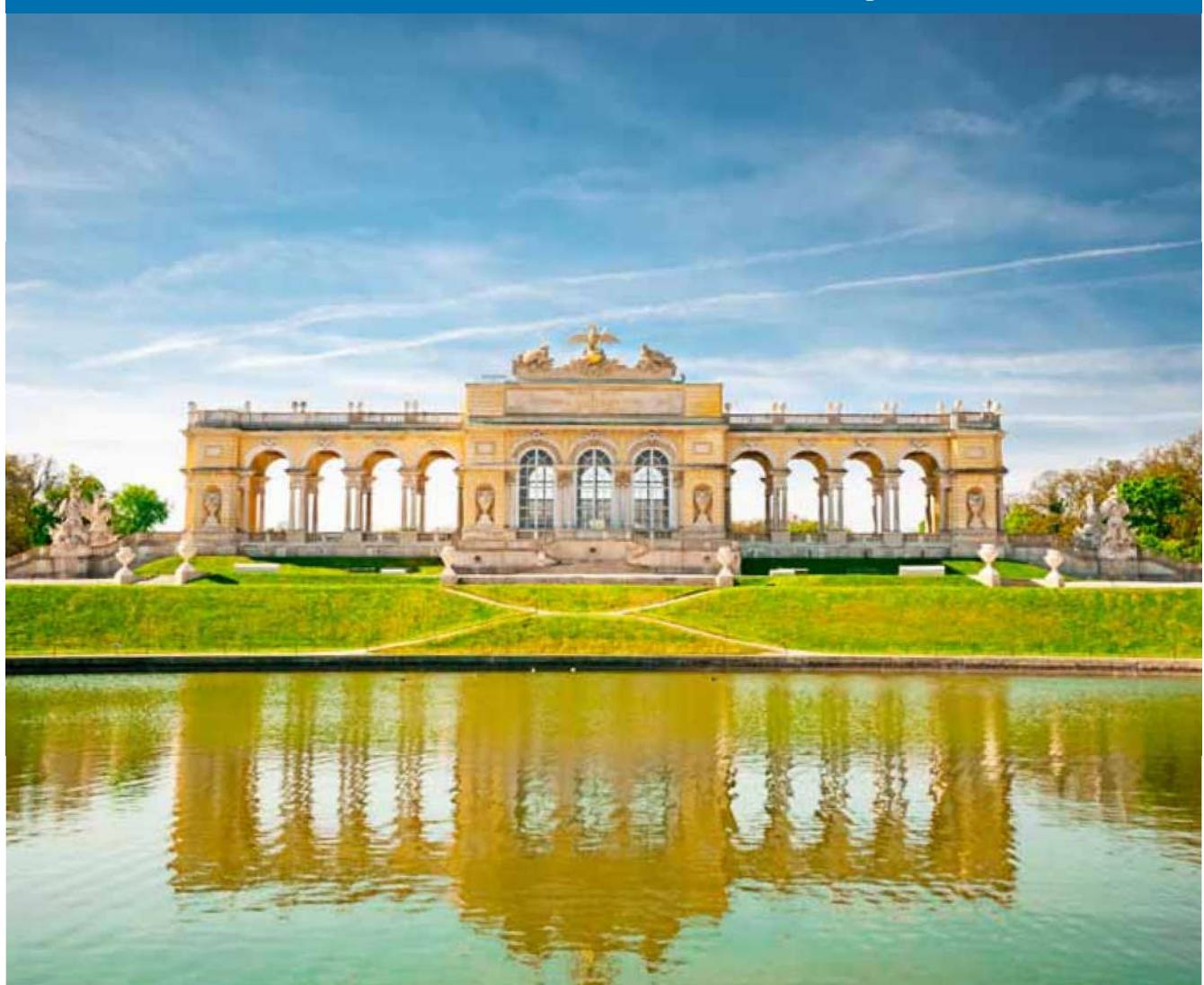
ESOC

2019

21st European Symposium on Organic Chemistry

Vienna / Austria

July 14-18, 2019



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CATIONIC 1,2-SILYL SHIFT IN PROPARGYL SILANES

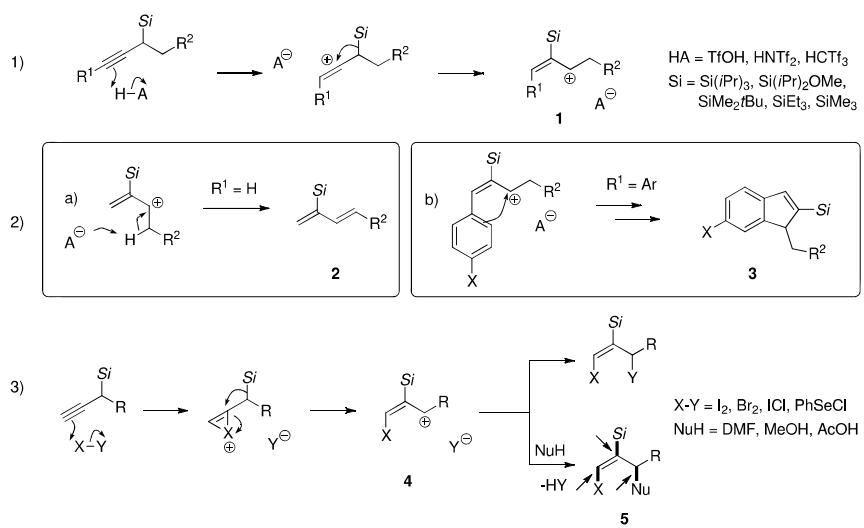
Mikus Purinš and Māris Turks

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Transformations involving non-vertical stabilization type 1,2-silyl shift in propargyl silanes give access to multi-functionalized products containing useful alkenyl silane moiety. Apart from the early reports of Danheiser [1] and Evans [2], this approach is still largely underdeveloped.

We have found that protonated propargyl silanes undergo 1,2-silyl shift, which results in an intermediate allyl carbenium ion 1. We demonstrate two possible reactivities of the reactive intermediate – elimination to give silyl dienes 2 and intramolecular Friedel-Crafts reaction to give silyl indenes 3 [1].

Using electrophilic halogen reagents such as *N*-bromosuccinimide the intermediate carbenium ion 4 can be intercepted by external nucleophile, i. e., solvent. This strategy allows for preparation of compounds 5 with up to 3 potential handles for further functionalization via palladium catalyzed cross-coupling chemistry.



[1] Danheiser, R. L.; Dixon, B. R.; Gleason, R. W. *J. Org. Chem.* **1992**, *57* (23), 6094–6097.

[2] Evans, D. A.; Aye, Y. *J. Am. Chem. Soc.* **2007**, *129* (31), 9606–9607.

[3] Purinš, M.; Mishnev, A.; Turks, M. *J. Org. Chem.* **2019**, *84* (6), 3595–3611.