Inducing 1,2-Silyl migration in propargyl silanes for the synthesis of 5- and 6-membered heterocycles

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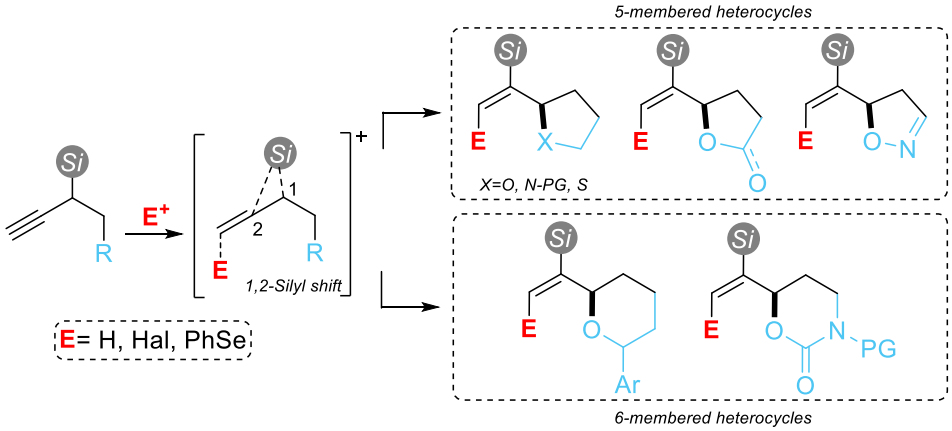
Electrophilic activation of propargyl silanes is known to induce the 1,2-silyl shift,[1] liberating stabilized allylic cations as intermediates. In previous studies these cationic intermediates have been subjected to 1) deprotonation for the synthesis of silyl dienes[2] (occurs in the absence of strong nucleophiles (R=alkyl, aryl)) and 2) reaction with external nucleophiles, resulting in 1,3-difunctionalization.[3]

In this work we demonstrate the use internal nucleophiles (*O-, S-, N-*) to trap the *in situ* generated intermediate allylic cations, leading to the formation of 5- and 6-membered heterocycles with a highly stereodefined olefin side chain (scheme 1). Various electrophiles, such as Brønsted acids (HOTf, $HNTf_2$), electrophilic halogen sources ($TsNBr_2$, NBS, NIS) and selenyl chloride (PhSeCl), were used to induce this transformation, providing diverse functionalization for the resulting olefin side chain. The synthetic utility of the obtained products was demonstrated by double-bond geometry-preserving electrophilic substitution (C=C-*Si* → C=C-Hal) and cross-coupling reactions (C=C-Hal → C=C-Aryl), giving access to styrene derivatives.[4]



Scheme 1. Heterocycle synthesis from propargyl silanes.

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REFERENCES

(1) Beļaunieks, R.; Puriņš, M.; Turks, M. Manifestation of the β-Silicon Effect in the Reactions of Unsaturated Systems Involving a 1,2-Silyl Shift. *Synthesis (Stuttg).* **2020**, *52* (15), 2147–2161.

(2) Puriņš, M.; Mishnev, A.; Turks, M. Brønsted Acid Catalyzed 1,2-Silyl Shift in Propargyl Silanes: Synthesis of Silyl Dienes and Silyl Indenes. *J. Org. Chem.* **2019**, *84* (6), 3595–3611.

(3) Beļaunieks, R.; Puriņš, M.; Līpiņa, R. A.; Mishnev, A.; Turks, M. 1,3-Difunctionalization of Propargyl Silanes with Concomitant 1,2-Silyl Shift: Synthesis of Allyl Functionalized Vinyl Silanes. *Org. Lett.* **2023**.

(4) Kroņkalne, R.; Beļaunieks, R.; Ubaidullajevs, A.; Mishnev, A.; Turks, M. 1,2-Silyl Shift-Induced Heterocyclization of Propargyl Silanes: Synthesis of Five-Membered Heterocycles Containing a Functionalized Olefin Side Chain. *J. Org. Chem.* **2023**, *88* (19), 13857–13870.