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USE OF PROPARGYLSILANES FOR THE PREPARATION OF HIGHLY FUNCTIONALIZED ALKENES VIA 1,2-SILYL MIGRATION

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The ease of the unsaturated system reactivity proceeding via β -silyl carbocation ion can be explained by the stabilizing effects of the silicon-carbon bond interaction with carbocation ion - known as β -silicon effect. This can be achieved by either vertical (hyperconjugation) or non-vertical (formation of cyclic silyonium ion) stabilization. The formation of the latter, in combination with other stabilizing effects, causes 1,2-silyl migration [1].

Previously, we have reported the use of Brønsted acid to catalyze reactions of propargyl silanes to form various silyl dienes and indenenes [2,3]. Herein, we report the expanded use of the concept by using electrophilic bromine to induce the formation of the reactive allylic cation that readily reacts with a variety of nucleophilic solvents like methanol, dimethylformamide, and acetic acid to form allyl functionalized vinyl silanes.

Use and the functionality of the obtained vinyl silanes are showcased in a variety of transition metal-catalyzed transformations like Suzuki-Miyaura coupling, C-H activation, electrophilic silicon exchange reaction, and Lewis acid-promoted intramolecular cyclization to form indenenes.

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