

View Abstract

ABSTRACT SYMPOSIUM NAME: New Reactions & Methodology

ABSTRACT SYMPOSIUM PROGRAM AREA NAME: ORGN

CONTROL ID: 3915259

PRESENTATION TYPE: Oral Preferred : Consider for Sci-Mix

TITLE: Synthesis of allylic systems or heterocycles with highly functionalized olefin side chain from propargyl silanes via 1,2-silyl migration

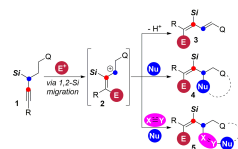
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ABSTRACT BODY:

Abstract: A non-vertical stabilization of β -silyl carbocations (formation of cyclic silonium ion) can lead to 1,2-silyl migration. Recently, we have applied this phenomenon in the Brønsted acid catalyzed synthesis of silyldienes **3** from propargylsilanes **1** ($E^+ = H^+$).

Herein, we report a further development of this methodology, which profits from the vinyl cation - allyl cation rearrangement via 1,2-silyl shift. Electrophiles like H^+ , Br^+ , I^+ , $PhSe^+$ and *in situ* generated organocopper(III) species can be used for the transformation $1 + E^+ \rightarrow 2$. The latter is prone to accept various nucleophiles in either intramolecular or intermolecular manner. These include alcohols, carboxylic acids, oximes, acyl and sulfonyl amides, carbamates and thioacetates. In this way highly functionalized allylic systems or heterocycles with substituted olefin side chain are obtained. The latter are shown to undergo further transformations by reactions like C-C cross-coupling reactions of vinyl halide or vinyl silane moieties, and allylic substitution. We have also extended this methodology to multicomponent approach by combining propargyl silane, incoming electrophile and nitrile for the Ritter type process, which is terminated by nucleophilic attack. Preliminary studies suggest that the transformation $1 \rightarrow 4$ can be performed in the enantioselective fashion in the presence of chiral Brønsted acids.



Presentation Preference: I wish to participate in an in-person session in San Francisco.

