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BRØNSTED ACID CATALYSED 1,2-SILYL SHIFT IN PROPARGYL SILANES

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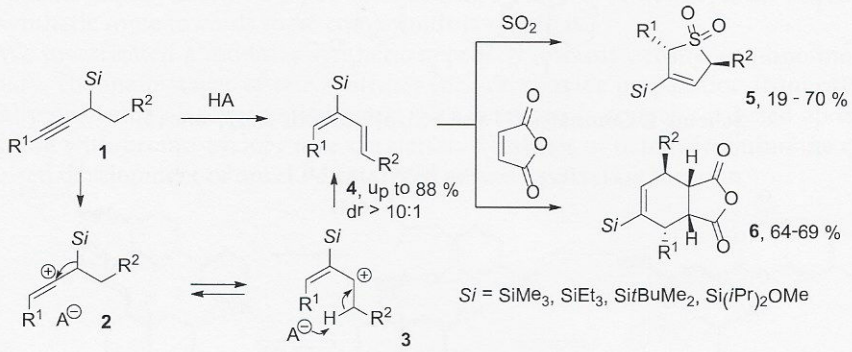
There are two possible pathways for propargyl silane reactions with electrophiles. The first involves Hosomi-Sakurai type aditition to aldehydes and imines. However, the second pathway involves migration of silyl group in the intermediate β-silyl vinyl carbenium ion and subsequent cyclization [1]. In such cases propargyl silanes act a 3-carbon unit in [3+2] annulation reactions.

Silyl dienes have proven to be versatile substrates, as they readily undergo cycloaddition reactions yielding vinyl silane moiety. Furthermore such products can participate in HiyamaDenmark cross-coupling reactions by transmetalation of the silyl group [2].



Scheme 1. Mechanism 1,2-silyl shift

Here we report the use of strong Brønsted acids such as triflic acid to activate the triple bond and promote 1,2-silyl shift in propargyl silanes. Deprotonation of the resulting allyl carbenium ion provides 2-silyl-1,3-dienes in good yields. Addition of dienophiles to silyl dienes yields Diels-Alder adducts in one pot procedure. Performing this rearrangement in liquid sulfur dioxide as a polar reaction medium [3, 4, 5], it is possible to activate the triple bond even with weak Brønsted acids such as benzoic acid.

References:

[1] Danheiser, R. L., Dixon, B. R., Gleason, R. W. *J. Org. Chem.* **1992**, *57*(23), 6094–6097.
[2] Choudhury, P., Welker, M. *Molecules.* **2015**, *20*(9), 16892–16907.
[3] Posevins, D., Suta, K., Turks, M. *Eur. J. Org. Chem.* **2016**, *2016*(7), 1414–1419.
[4] Luginina, J., Uzuleņa, J., Posevins, D., Turks, M. *Eur. J. Org. Chem.* **2016**, *2016*(9), 1760–1771.
[5] Luginina, J., Turks, M. *Synlett.* **2017**, *28*(8), 939–943.