Synthesis of Silyl Dienes from Propargyl Silanes

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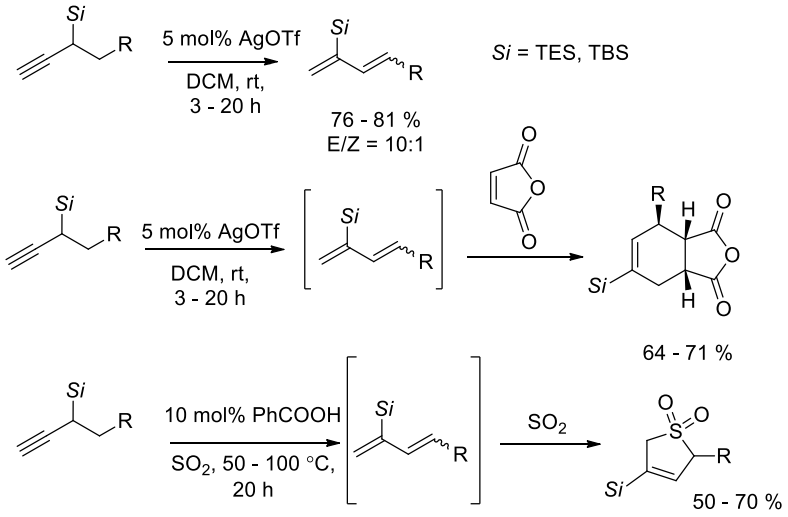
Propargyl silanes are useful synthetic intermediates mainly used in Sakurai type addition to aldehydes or imines. However, there are some reports on propargyl silanes as a 3 carbon unit in [3+2] annulation reactions. Such reactions involve migration of silyl group in the intermediate *β*-silyl vinyl carbenium ion and subsequent cyclization [1].

Silyl dienes are versatile substrates used in cycloaddition reactions. These adducts are further exploited as vinyl silanes in electrophilic substitution or Hiyama-Denmark cross coupling-reactions [2].

Here we report the use of *π*-selective Lewis acid silver triflate to activate the triple bond and promote 1,2-silyl shift. Deprotonation of the resulting allyl cation and protodemetallation provides 2-silyl-1,3-dienes in good yields. Addition of dienophiles to silyl dienes provides Diels Alder adducts in one pot procedure. Performing this rearrangement in liquid sulfur dioxide as a polar reaction medium, it is possible to activate the triple bond even with weak Brønsted acids such as benzoic acid.



Literature:

[1] R. L. Danheiser, B. R. Dixon, R. W. Gleason, J. Org. Chem. 1992, 57, 6094. [2] P. P. Choudhury, M. E. Welker, Molecules 2015, 20, 16892.