

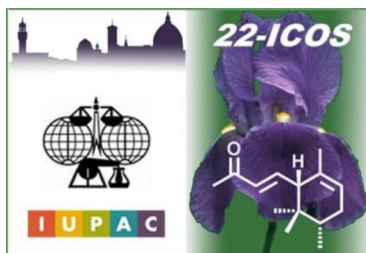
XXII International Conference on Organic Synthesis

16-21 September 2018, Florence, Italy



SCIENTIFIC PROGRAM & ABSTRACT BOOK

<http://www.22-icos-florence.it/>



XXII International Conference on Organic Synthesis (22-ICOS)

Contents

Welcome to 22-ICOS

Organizers and Committees

Venue

About Iris

Thieme IUPAC prize 2018

Sponsors

Scientific program and social events

Plenary Lectures (PL).....PL1-PL12

Invited Lectures (IL).....IL1-IL17

Keynote Lectures (KL).....KL1-KL3

Oral Communications (OC).....OC1-OC66

Poster Session A.....FLP1-FLP6, P1-P170

Poster Session B.....FLP7-FLP12, P171-P340

Poster Session C.....FLP13-FLP19, P341-P503

Index of Authors

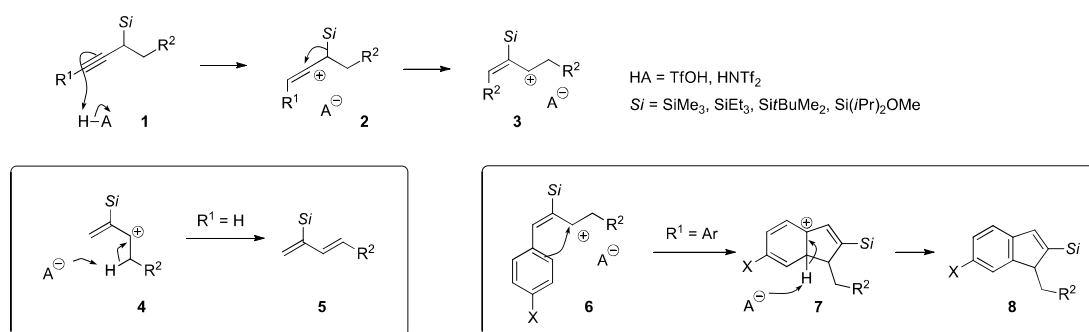
Synthesis of Silyl Dienes and Indenes via 1,2-Silyl Shift

Mikus Puriņš, Māris Turks

Institute of Technology of Organic Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena str. 3, Riga, LV-1048, Latvia, mikus.purins@rtu.com

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

Vinyl silanes have always been attractive building blocks to organic chemists due to the nature of the carbon silicon bond. Vinyl silanes can participate as nucleophilic partners either in electrophilic substitution or Pd catalyzed cross-coupling reactions. Silyl dienes have proven to be versatile substrates, as they readily undergo cycloaddition reactions yielding vinyl silane moiety [2]. Indene carbocyclic skeleton has found recent applications in materials science [3].



Scheme 1. 1,2-Silyl shift in propargyl silanes.

Here we report the use of strong Brønsted acids such as triflic acid to protonate the triple bond in propargyl silanes **1**. Resulting β -silyl vinyl carbenium ion **2** undergoes 1,2-silyl shift to give more stable β -silyl allyl carbenium ion **3**. Protodesilylation is largely suppressed by usage of bulky silyl groups. Allyl carbenium ions **4** generated from terminal propargyl silanes undergo deprotonation to give silyl dienes **5**. For 1-aryl propargyl silanes a competing intramolecular Friedel-Crafts alkylation in the intermediate carbenium ion **6** is observed. Careful investigation of reaction conditions revealed that more polar solvents and less coordinating acid anion favor silyl indene **8** formation. Further application of unsaturated silanes is also demonstrated. Silyl dienes easily participate in Diels-Alder cycloadditions in one pot procedure. Diisopropylmethoxysilyl diene can also be used in Hiyama-Denmark cross coupling reaction. When performing this rearrangement in liquid sulfur dioxide as a polar reaction medium [4, 5, 6], 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. He, Y.; Chen, H.; Hou, J.; Li, Y. *J. Am. Chem. Soc.* **2010**, 132 (4), 1377. 4. Posevins, D.; Suta, K.; Turks, M. *Eur. J. Org. Chem.* **2016**, 2016 (7), 1414–1419. 5. Lugiņina, J.; Uzuleņa, J.; Posevins, D.; Turks, M. *Eur. J. Org. Chem.* **2016**, 2016 (9), 1760–1771. 6. Lugiņina, J.; Turks, M. *Synlett* **2017**, 28 (8), 939–943.