

Analysis of Synthetic Routes toward Allenylsilanes



Biography

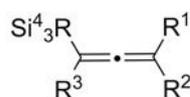
Valentin Bochatay obtained his master's degree in 2013 from the University Pierre et Marie Curie, Paris. One of his postgraduate projects was spent in Prof. John A. Murphy's group under the supervision of Dr. Stuart Lang at Strathclyde University, Glasgow and examined palladium-catalyzed processes for the synthesis of benzothiazoles. He is currently engaged in his PhD. in Prof. Fabrice Chemla's group under the guidance of Prof. Franck Ferreira and Dr. Alejandro Pérez Luna focusing on the synthesis and use of 4-amino-1-allenylsilanes.

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Abstract

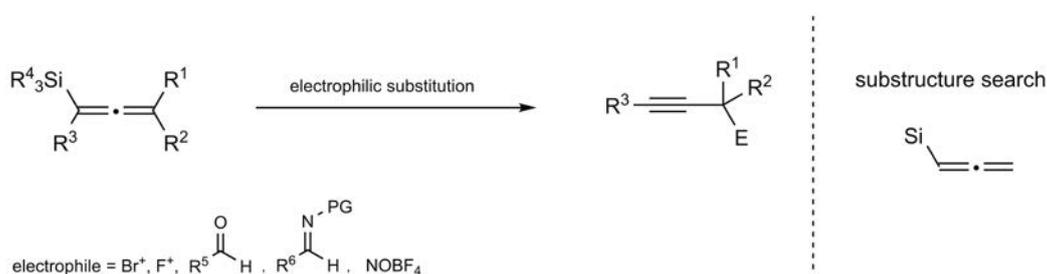
In this case study, we investigated possible synthetic approaches toward allenylsilanes (Scheme 1) using *Science of Synthesis Online*. The survey provided a general and comprehensive picture of the available routes presented in a clear and synthetic way.



Scheme 1 General Structure of Allenylsilanes

Discussion

One of the research axes of our group is devoted to studying the preparation and synthetic applications of allenyl/propargyl metal reagents. As part of this work, we recently became interested in analogous nucleophiles derived from metalloids because they offer the potential to develop well-defined, isolable, easy-to-handle reagents. Allenylsilanes represent a well-established family of such compounds. They are, in fact, known to be useful synthons that react by electrophilic substitution with a variety of electrophiles, including for instance aldehydes and imines (Scheme 2).



Scheme 2 Electrophilic Substitution of Allenylsilanes and Substructure Search Used

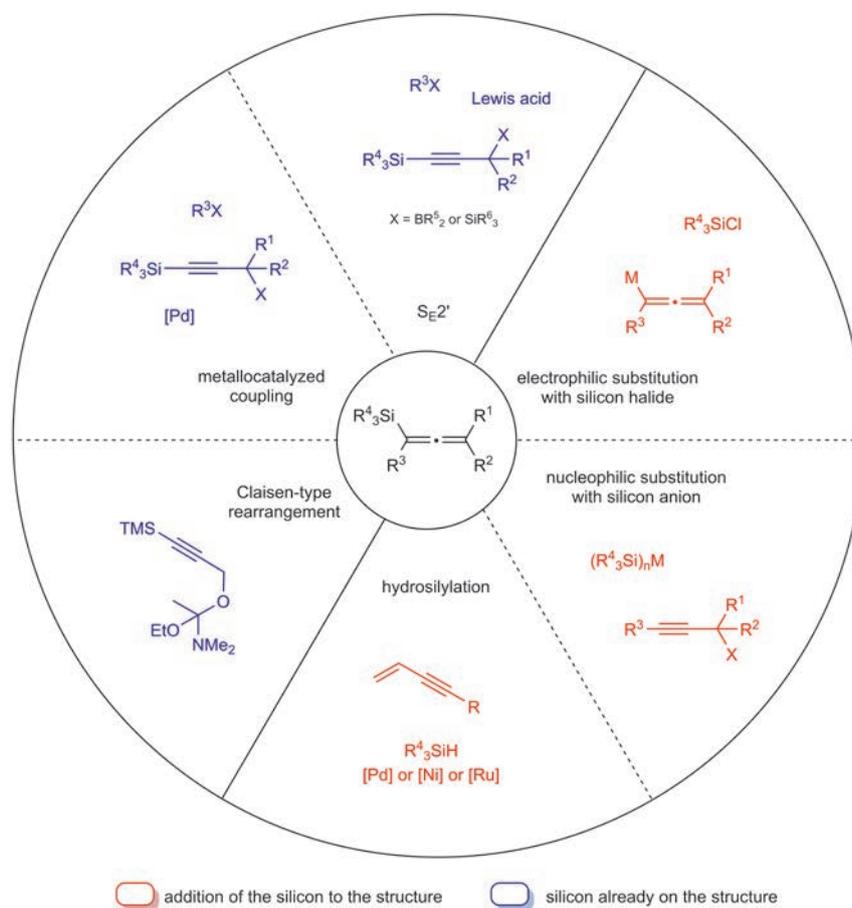
Being aware of the synthetic potential of allenylsilanes, we searched *Science of Synthesis Online* for synthetic approaches to this substrate class. We started by performing a substructure search with the structure depicted in Scheme 2 that provided 165 hits that were further reduced to 119 after filtering the result with the "Reaction Product" tool. This first result set provided a large view of reported reactions in which the final compound contains an allenylsilane moiety. In order to identify the synthetic procedures specifically designed to prepare allenylsilanes, we then selected the results including the term "allenylsilane" in the full text. This final result set contained a reasonable number of 30 hits and

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could therefore be analyzed readily with the navigation tool in order to obtain an overview in which the most general methods could be discriminated from the more specific ones.

From our own experience, we already knew some general approaches to allenylsilanes, such as the S_N2' displacement of propargylic leaving groups by silicon anions (silylzincates and silylcuprates) or the silylation of main-group allenylmetal reagents (Scheme 3). We were however pleased to note that other methods such as metal-catalyzed cross-coupling of silylated propargylic halides, metal-catalyzed hydrosilylation of 1,3-enynes or S_E2' electrophilic substitution of silylated propargylic boranes and propargylic silanes are also broad in scope and thus offer interesting additional opportunities. We also found that Claisen-type rearrangements provide a facile and quite general entry to allenylsilanes, even though the access to the substrates required for the preparation of a given target can limit the applicability of this approach. Other less widespread synthetic routes such as carbene dimerization, silylboration of 1,3-enynes, or the Wittig reaction between a phosphorus ylide and a (trialkylsilyl)ketene were also identified and completed the overall picture.



Scheme 3 Synthetic Approaches toward Allenylsilanes Classified According to Reactivity-Based Subclasses

Conclusion

Science of Synthesis Online easily gave us a convenient overview of the synthetic approaches to allenylsilanes. Besides the clear and schematic tree structure in which the organic transformations are organized, the presence of general procedures enhanced by information on potential hazards enabled selection of the most suitable and efficient synthetic pathways toward a desired target