

# SYNLETT Spotlight

## Applications of Allenylsilanes in Organic Synthesis

Compiled by Sharada Prasanna Swain



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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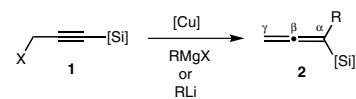
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### Introduction

Allenylsilanes **2** are versatile reagents widely used in organic synthesis.<sup>1</sup> Generally, allenylsilanes react as propargyl anion equivalents in Lewis acid mediated<sup>2</sup> or thermal<sup>3</sup> nucleophilic addition to electrophiles such as carbonyls, imines, Selectfluor, and *N*-bromosuccinimide, etc.<sup>1,4,5</sup> The regioselective addition of allenylsilanes provides a  $\beta$ -vinyl cation, which is stabilized by a C–Si bond, which is called  $\beta$  effect. The C–Si bond in allenylsilanes is oriented cisoplanar to the *p*-orbital of the carbocation and provides direct stabilization.<sup>5</sup> Allenylsilanes undergo [3+2] annulations with  $\alpha,\beta$ -unsaturated carbonyls, carbonyl compounds, imines, and nitrosyl cations to form cyclo-

pentenones, dihydrofurans, dihydropyrroles, and isoxazoles, respectively.<sup>1,4,5</sup>

The efficient methods for the synthesis of allenylsilanes **2** are copper-mediated 1,3-substitution reactions of carbon nucleophiles to propargylic substrates **1** having a leaving group at the propargylic position.<sup>6,7</sup>



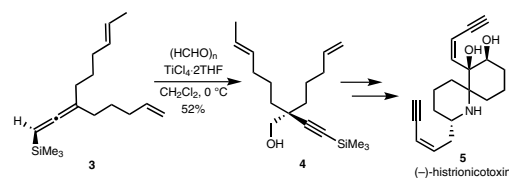
[Si] = SiMe<sub>3</sub>, TBDMS, TBDPS, etc.

X = OMs, OAc, etc. R = alkyl, aryl

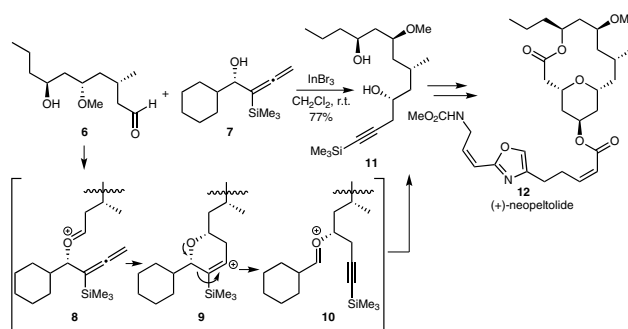
**Scheme 1** Synthesis of allenylsilanes

### Abstracts

(A) *Reactions with Aldehydes:* Allenylsilanes react with aldehydes and ketones in the presence of titanium tetrachloride to provide homopropargylic alcohols in a regioselective manner. The reaction of chiral allenylsilanes with chiral aldehydes leads to the formation of mainly *syn* homopropargylic alcohols.<sup>3</sup> The reaction of chiral 3,3-disubstituted allenylsilane **3** with paraformaldehyde in the presence of TiCl<sub>4</sub>·2THF generates chiral homopropargylic alcohol **4**, which is the key intermediate in the total synthesis of (–)-histrionicotoxin **5**.<sup>8</sup>



(B) *Reactions with Aldehydes:* The reaction of chiral 2-silyl-substituted  $\alpha$ -allenlic alcohol **7** with aldehyde **6** in the presence of InBr<sub>3</sub> give rise to chiral homopropargylic alcohol **11**. The reaction proceeds via formation of oxocarbenium ion **8**, which undergoes a [3,3]-sigmatropic rearrangement to form the alcohol **11**. The alcohol **11** is the key intermediate in the total synthesis of the natural product (+)-neopeltolide **12**.<sup>9</sup>



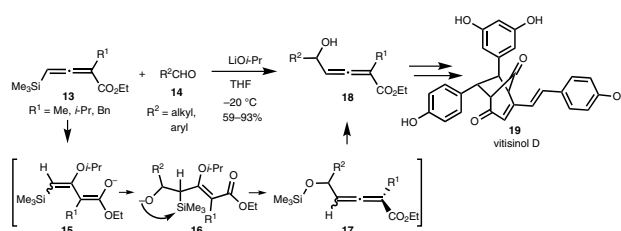
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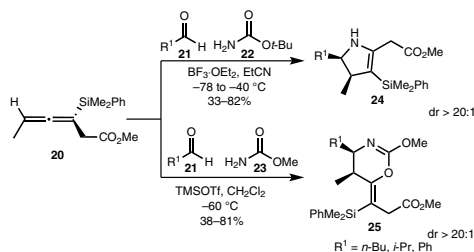
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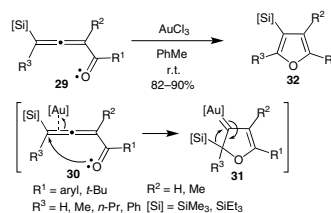
(C) *Reactions with Aldehydes*: The addition of  $\gamma$ -trimethylsilyl alene esters **13** to aldehydes **14** in the presence of *i*-PrOLi leads to the formation of regioselective  $\gamma$ -carbinols **18**. The addition of anionic catalyst *i*-PrOLi leads to the intermediate **15**, which possess enolate-like reactivity. The nucleophilic addition of intermediate **15** to aldehyde **14** generates intermediate **16**. Then, the silyl group undergoes a 1,3-shift and the nucleophile eliminates to form the intermediate **17**. This reaction is the key step in the total synthesis of the [3.2.1] bicyclic natural product vitisinol D.<sup>10</sup>



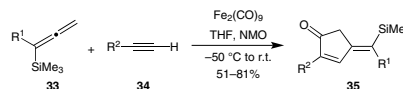
(D) *Reactions with Imines*: The enantioenriched allenylsilane **20** reacts with the in situ generated iminium ion generated from *t*-butyl carbamate **22** and aldehydes **21** in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$  to form substituted 4,5-dihydropyrroles **24**. Similarly, the reaction of allenylsilane **20** with an iminium ion, generated in situ from methyl carbamate **23** and aldehydes **21** in the presence of TMSOTf, forms substituted 4,5-dihydrooxazines **25**.<sup>11</sup>



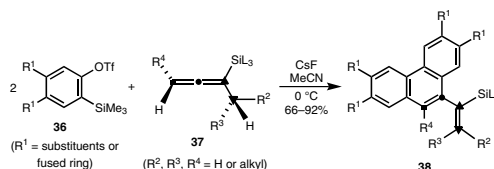
(E) *Gold-Catalyzed Cycloisomerization*: In the presence of  $\text{AuCl}_3$  the  $\gamma$ -silyl-substituted allenyl ketones **29** undergoes cycloisomerization to 3-silyl furans **32**. The cyclization of the allenyl ketone **29** give rise to the intermediate gold-carbene **31**, and upon the 1,2-Si shift, the 3-silyl furan **32** is produced.<sup>12</sup>



(F) *The Pauson–Khand Reaction of 1,1-Disubstituted Allenylsilanes*: The Pauson–Khand reaction of 1,1-disubstituted allenylsilanes with terminal alkynes leads to 4-alkylidene-2-cyclopenten-1-ones in good yields. The reaction proceeds through a [2+2+1] pathway. A three-membered iron metacycle is generated by reaction of allenylsilane **33** with diiron nonacarbonyl. The iron metacycle undergoes complexation with alkyne **34**, and finally, a reductive elimination takes place to provide the 4-alkylidene-2-cyclopenten-1-one **35**.<sup>13</sup>



(G) *[2+2+2] Cycloaddition with Benzenes*: Benzenes possess a strained triple bond and are highly electrophilic. Allenylsilanes **37** react with two equivalents of benzenes **36** to generate ( $\alpha$ -phenanthrenyl)vinylsilanes **38** in excellent yields. The reaction proceeds through a [2+2+2] pathway.<sup>14</sup>



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