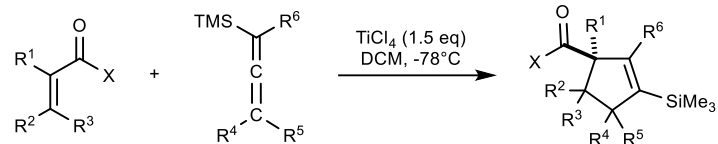


General Reaction Scheme

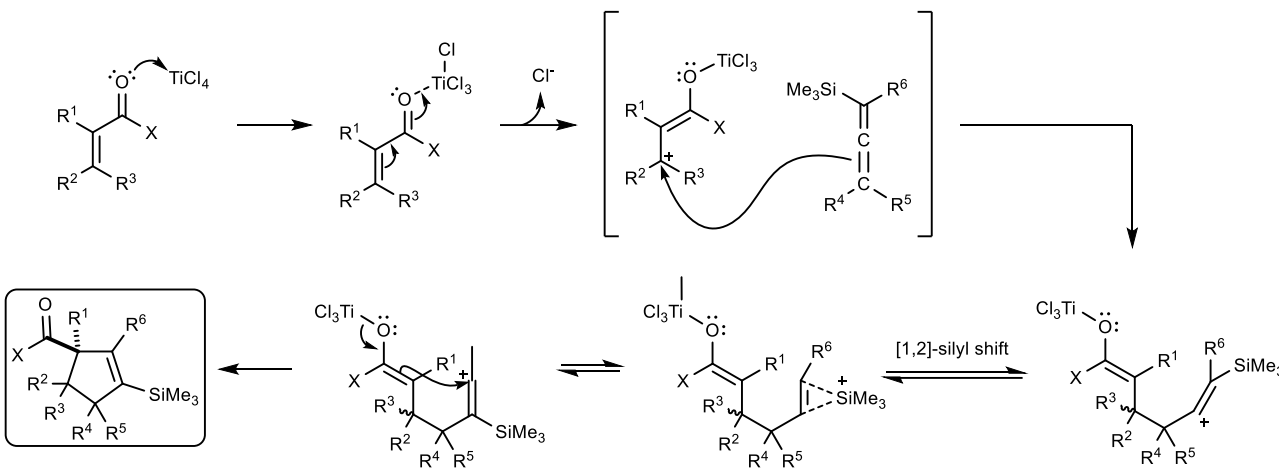


The Danheiser Cyclopentene annulation is the (3+2) cyclization of trimethylsilyl allenes with electron-deficient olefins to generate cyclopentenes.

The reaction is both stereo- and regioselective, favoring suprafacial addition of the allene to the allenophile.

Guiding overview: Ch. 3.1 Danheiser Annulation. In *Name Reactions for Carbocyclic Ring Formations*, Wiley, Ed. 2010; pp 72-92.

Mechanism

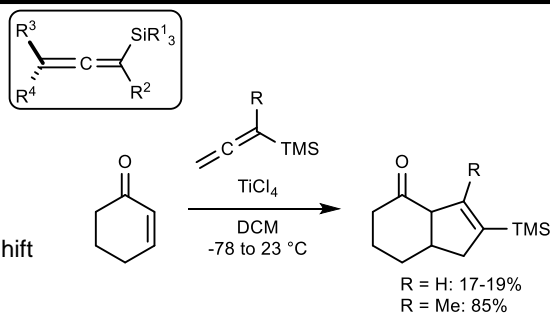


J. Am. Chem. Soc. **1981**, *103*, 1604. <https://doi.org/10.1021/ja00396a071>

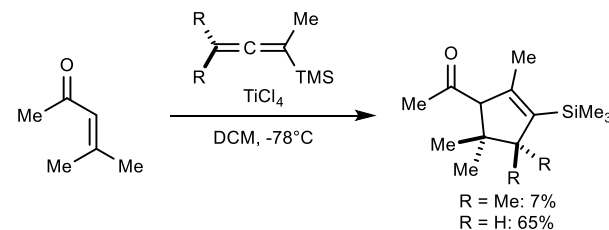
Scope: Silyl allenes

Substitution at R² is required for synthetically useful yields.

This is attributed to the relative stability of the carbocation intermediate during the [1,2] silyl shift (above).

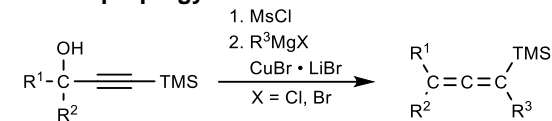


Substitution at R³ and R⁴ may impact yield in extremely hindered substrates.



Preparation of TMS allenes:

From propargyl alcohols:



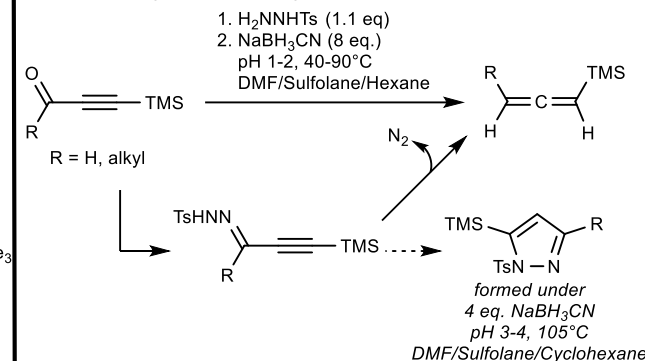
J. Am. Chem. Soc. **1981**, *103*, 1604.

<https://doi.org/10.1021/ja00396a071>

Synthesis **1979** *5*, 390.

<https://doi.org/10.1055/s-1979-28697>

From ynones and ynals:



Tetrahedron **1983**, *39*, 935.

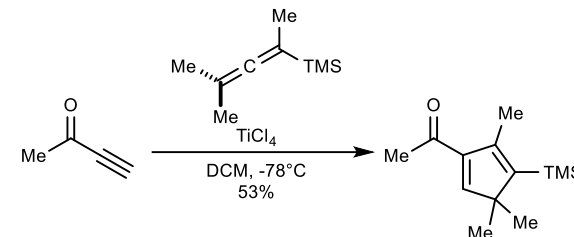
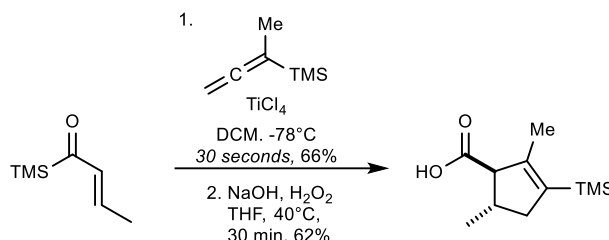
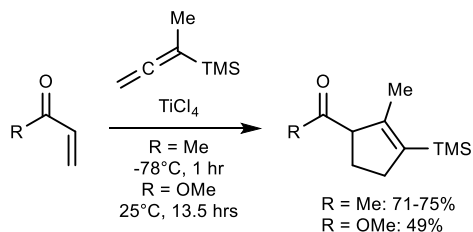
[https://doi.org/10.1016/S0040-4020\(01\)88592-6](https://doi.org/10.1016/S0040-4020(01)88592-6)

Tetrahedron **1983**, *39*, 935. [https://doi.org/10.1016/S0040-4020\(01\)88592-6](https://doi.org/10.1016/S0040-4020(01)88592-6)

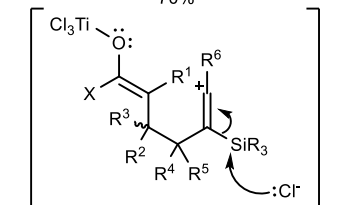
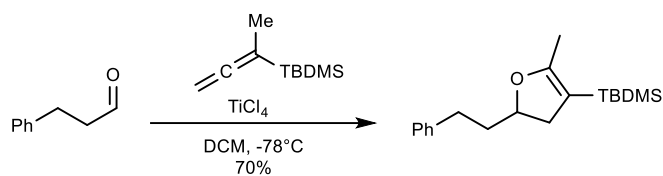
Scope: Electrophiles

Esters are tolerated, albeit at much slower reaction rates than ketones. Carboxylic acids will not react, although the analogous product can be formed from a two-step procedure beginning with an acyl silane:

Propargylic ketones can be used to form cyclopentadienes:

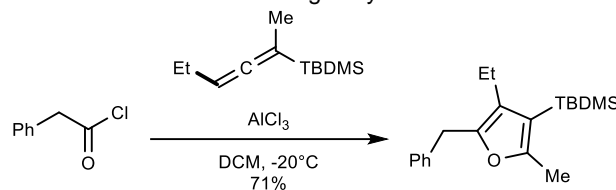


With the use of bulky silanes to discourage desilylation, aldehydes can form dihydrofurans:

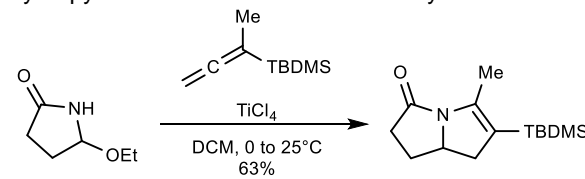


Desilylation disfavored in bulkier silanes

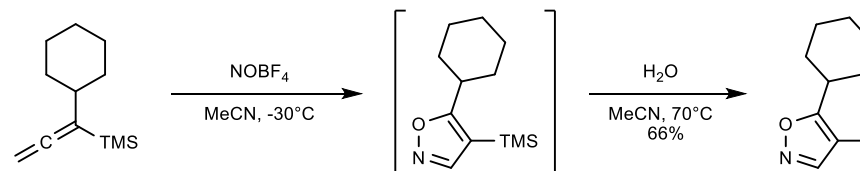
Furans are accessed through acyl chlorides:



Dihydropyrroles can be formed from *N*-acyliminium ions:



The use of nitronium as an electrophile gives isoxazoles:



Limitations:

α,β -unsaturated aldehydes will give a complex mixture of products, whereas some electron-deficient as nitroalkenes will give acyclic products as a result of desilylation.

Enantioselective variants for this transformation have been reported.

Towards dihydrofurans:
J. Am. Chem. Soc. **2001**, 123, 12095.

<https://doi.org/10.1021/ja011983i>

Towards dihydropyrroles:
Org. Lett. **2005**, 7, 1051.

<https://doi.org/10.1021/ol047343c>

Furans: *J. Am. Chem. Soc.* **1989**, 111, 4407. <https://doi.org/10.1021/ja00194a040>

Acyl Silanes: *Tetrahedron Letters* **1985**, 26, 2513. [https://doi.org/10.1016/S0040-4039\(00\)98824-5](https://doi.org/10.1016/S0040-4039(00)98824-5)

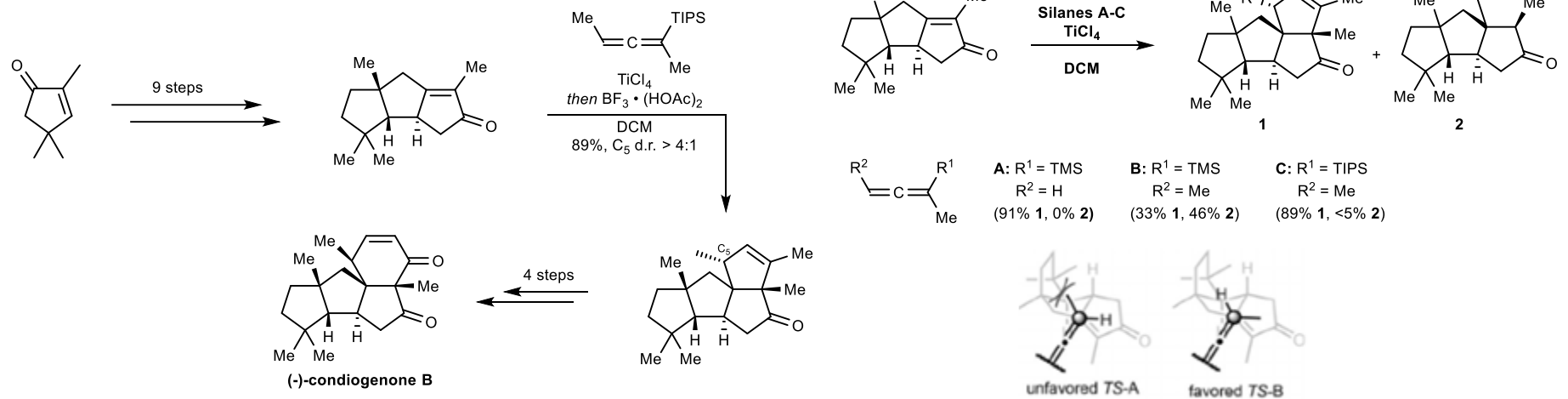
General Scope: *Tetrahedron* **1983**, 39, 935. [https://doi.org/10.1016/S0040-4020\(01\)88592-6](https://doi.org/10.1016/S0040-4020(01)88592-6)

Isooxazoles: *Heterocycles* **1987**, 25, 277. <https://doi.org/10.3987/S-1987-01-0277>

Dihydrofurans/pyrroles: *J. Am. Chem. Soc.* **1985**, 107, 7234. <https://doi.org/10.1021/ja00310a109>

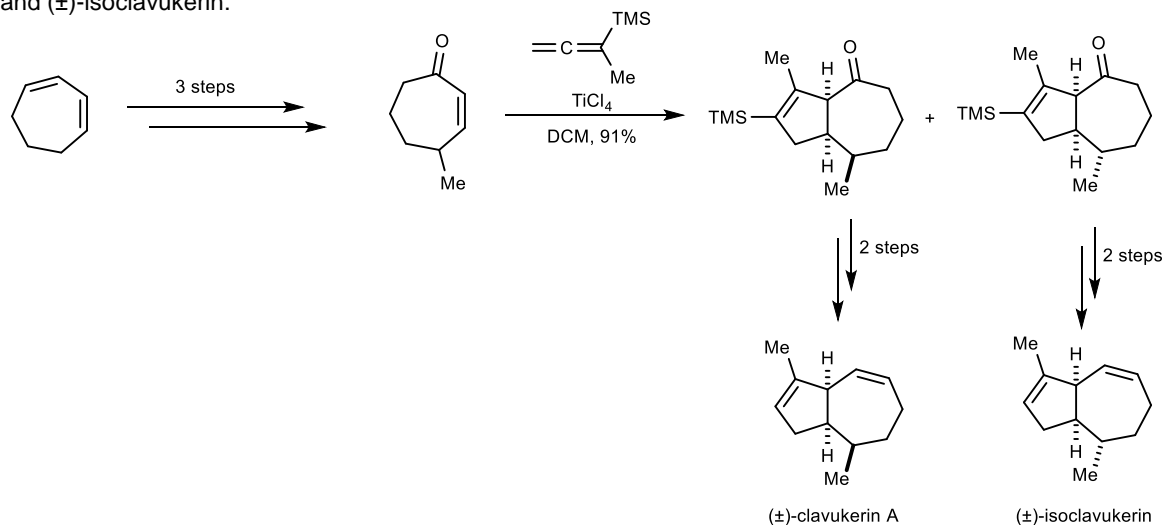
Applications in Total Synthesis:

Towards (-)-condiogenone B:



Angew. Chem. Int. Ed. 2020, 59, 1. <https://doi.org/10.1002/anie.202007247>

Towards (±)-clavukerin A and (±)-isoclavukerin:



Tetrahedron Letters 2002, 42, 2683. [https://doi.org/10.1016/S0040-4039\(02\)00402-1](https://doi.org/10.1016/S0040-4039(02)00402-1)