

Accessing Trimethylenemethane-Palladium Complexes with 2-Acetoxyethyl-3-allyltrimethylsilane

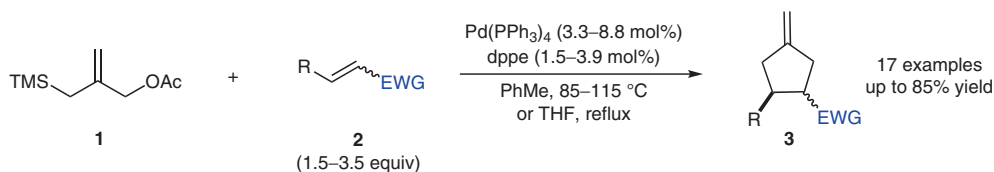
Category

Metals in Synthesis

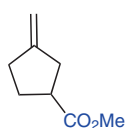
Key words

palladium catalysis
trimethylenemethane
[3+2] cycloaddition
2-acetoxyethyl-3-allyltrimethylsilane

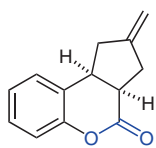
Synfact
Classic



Selected examples:

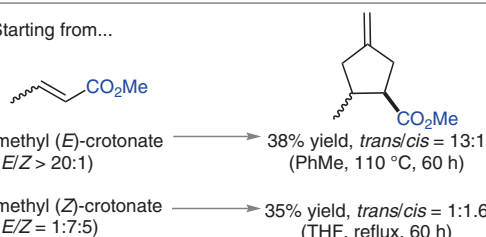


no dppe, PhMe, 85 °C
68% yield (43 h)

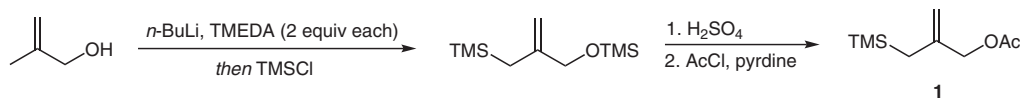


no dppe, PhMe, 115 °C
52% yield (14 h)

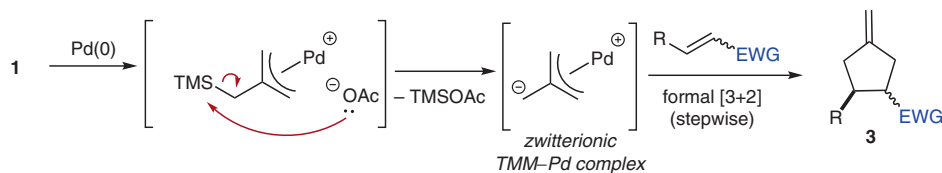
Starting from...



Synthesis of reagent 1:



Proposed mechanism:



Significance: In 1979, Trost and Chan reported the use of 2-acetoxyethyl-3-allyltrimethylsilane **1** as a reagent that can be activated by a palladium catalyst to achieve formal [3+2] cycloaddition with an olefin partner. Notably, reagent **1** can be easily synthesized from readily available α -methylallyl alcohol. The catalytic reaction involves the generation of a zwitterionic trimethylenemethane-palladium complex, which reacts with electron-deficient alkenes to form methylenecyclopentanes **3**. The lack of stereospecificity with stereodefined 1,2-disubstituted olefins, such as methyl-(*Z*)-crotonate, indicates that the formal [3+2] cycloaddition occurs in a stepwise fashion.

Comment: Since this seminal report, reagent **1** and similar silylated allyl acetates or carbonates have proven to be of high synthetic utility, with numerous applications in natural product synthesis. Notably, compatible 2π partners are not limited to electron-deficient olefins; aldehydes and imines can also be used (see Review below). Moreover, diastereoselective and enantioselective [3+2] cycloadditions with those reagents can also be enabled using chiral palladium catalysts.

Review: S. Yamago, E. Nakamura *Org. React.* **2002**, *61*, 1–217.