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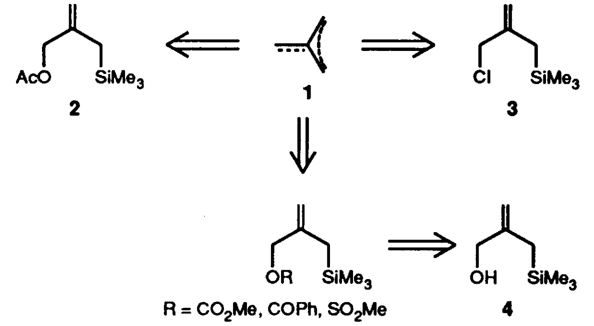
TMM Equivalents

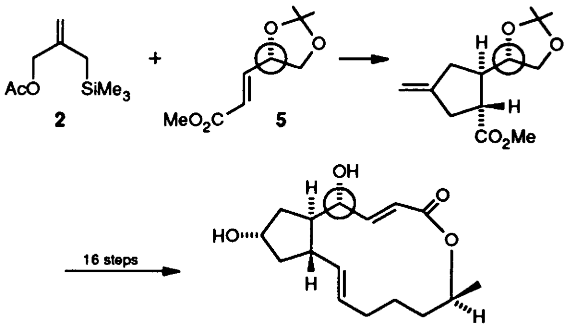
The [3 + 2] cycloaddition of TMM (trimethylenemethane, 1) and olefins is an important method of quinane (cyclopentane) annulation. Through the extensive efforts of Professor Barry Trost's group, this annulation method has now become a practical synthetic transformation promising widespread applicability in organic synthesis.



Previous attempts to capture TMM or stable TMM metal adducts usually resulted in poor yields and/or selectivity. The Trost modification uses silylated compounds **2** and **3** as well as carboxylate and sulfonate esters of **4**. These compounds provide convenient and stable (clear, colorless liquids at room temperature) alternatives to TMM metal adducts *or* the bicyclic azo adduct of TMM. The TMS group of **2** or **3** functions as a *carbanion-equivalent* site whereas the acetate or halide group functions as a *carbocation-equivalent* site. They are readily activated with catalytic quantities of palladium,[1] nickel[2] or molybdenum[3] salts and participate in the cycloaddition reactions as fleeting reactive intermediates. Retention of *E*-olefin geometry, high diastereoselectivity and good regioselectivity are some of the salient features of this method. The following examples illustrate the utility of these four-carbon synthons.

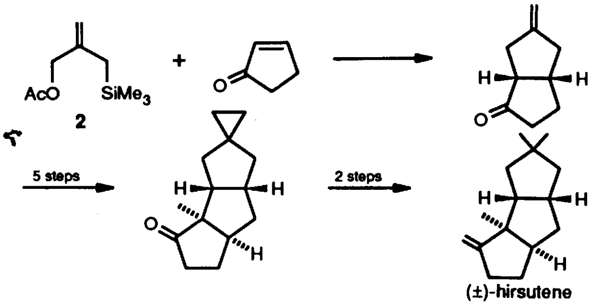
Synthesis of (+)-Brefeldin-A:[4]

The highly functionalized macrocyclic antibiotic, brefeldin-A, was prepared from **2** and **5** by Trost and co-workers in seventeen steps.



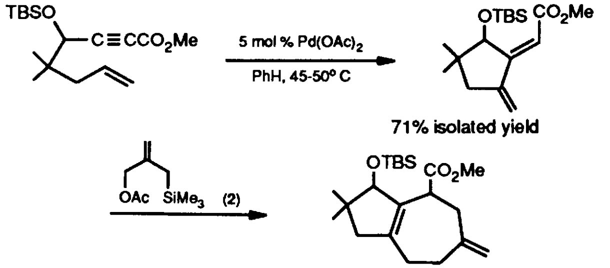
(±)-Hirsutene Synthesis:[1]

Binger and co-workers used the relatively easy conversion of an *exo*-methylene group to a *gem*-dimethyl group in developing a synthesis of hirsutene. The appropriate methylenecyclopentane intermediate was prepared utilizing the TMM cycloaddition method.



An Approach to Polyhydroazulenes:[5]

Trost and co-workers recently extended the TMM cycloaddition method to include the synthesis of a polyhydroazulene skeleton which is the core ring system for many natural products. The cisoid-diene component of this [4 + 3] cycloaddition was prepared using an interesting intramolecular ene-yne cyclization process.



71% isolated yield

2.4:1 mixture of seven-membered ring products

As illustrated above, the TMM cycloaddition is fast becoming a very useful method not only of methylenecyclopentannulation but also for synthesizing other useful skeletal fragments such as methylenepyrrolidines,[2a] tetrahydrofurans,[6] cyclopentenes,[7] and hydroazulenes.[5]

TMM equivalents are important and useful for organometallic chemists as well. Aldrich now offers reagents **2**, **3**, **4** and many other reagents used in Professor Trost's annulation chemistry.

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   c) Dubac, J. *et al. J. Organometal. Chem.* **1985**, *281*, 149.

33,983-0 2-[(Trimethylsilyl)methyl]-2-propen-1-yl acetate, 99% (2) 1g $20.50; 5g $69.00

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