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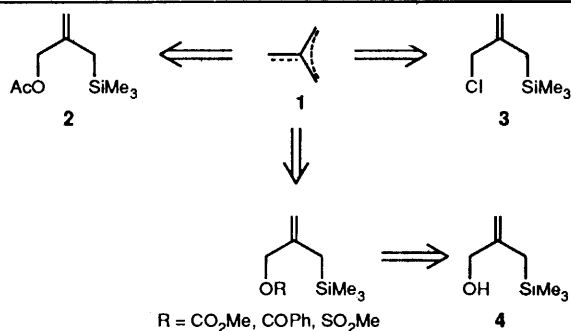
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# TMM Equivalents

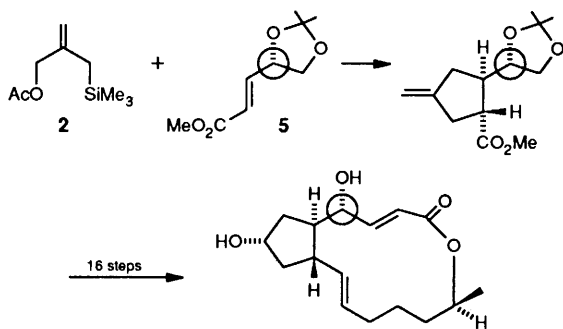
The [3 + 2] cycloaddition of TMM (trimethylenemethane, 1) and olefins is an important method of quinane (cyclopentane) annulation. Through the extensive efforts of Professor Barry Trost's group, this annulation method has now become a practical synthetic transformation promising widespread applicability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

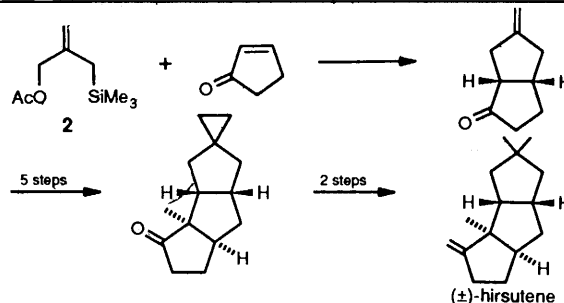
### Synthesis of (+)-Brefeldin-A:<sup>4</sup>

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



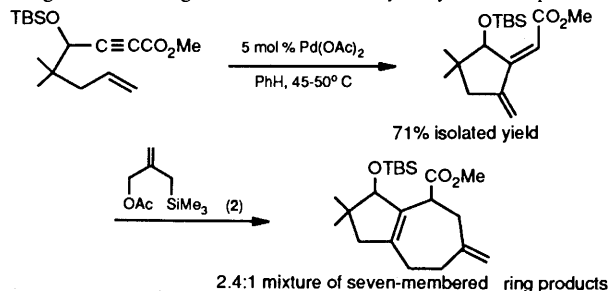
### (±)-Hirsutene Synthesis:<sup>5</sup>

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:<sup>5</sup>

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.



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,<sup>2a</sup> tetrahydrofurans,<sup>6</sup> cyclopentenes,<sup>7</sup> and hydroazulenes.<sup>5</sup>

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.

### References:

- 1) For a recent review on this subject, see Trost, B.M. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 1.
- 2) a) Jones, M.D.; Kemmitt, R.D.W. *Chem. Commun.* **1986**, 1201.  
b) Molander, G.A.; Shubert, D.C. *Tetrahedron Lett.* **1986**, 27, 787.
- 3) Trost, B.M.; Lautens, M. *J. Am. Chem. Soc.* **1987**, 109, 1469.
- 4) Trost, B.M.; Lynch, J.; Renaut, P.; Steinman, D.J. *ibid.* **1986**, 108, 284.
- 5) Trost, B.M.; MacPherson, D.T. *ibid.* **1987**, 109, 3483.
- 6) Trost, B.M.; King, S.A. *Tetrahedron Lett.* **1986**, 27, 5971.
- 7) Trost, B.M.; Balkovec, J.M.; Angle, S.R. *ibid.* **1986**, 27, 1445.
- 8) a) For a review, see Jones, M.D.; Kemmitt, R.D.W. *Adv. Organomet. Chem.* **1987**, 27, 279.  
b) Jones, M.D. *et al. Chem. Commun.* **1984**, 673  
c) Dubac, J. *et al. J. Organometal. Chem.* **1985**, 281, 149.

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