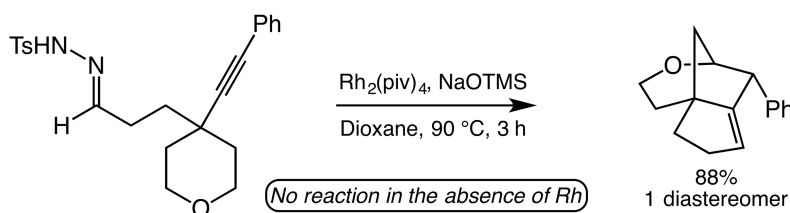


Synthetic Discoveries from Polycyclic Natural Products

Pr Jeremy MAY, University of Houston (USA)

In the pursuit of the synthesis of bridged polycyclic terpenoid natural products, a powerful carbene/alkyne cascade reaction has been discovered that forms multiple rings in a single reaction. This reaction proceeds from a diazoester or alkyl hydrazone to generate a carbene that reacts with an adjacent alkyne. Carbonyl azides can generate nitrenes that also initiate the cascade. The resulting reactive intermediates proceed through a transannular C-H bond insertion to generate bridged polycyclic products. Mechanistic intermediates and stereoelectronic effects have also been investigated and enantioselective transition metal catalysts designed.



In the pursuit of the synthesis of biologically active natural products (compounds originally isolated from natural sources), powerful reactions using organocatalytic or acid catalysts (i.e., metal-free) have allowed organoboronates to form new C–C bonds via cationic intermediates. The new chemical transformations thus made available, along with the extraordinary chemical compatibility the new catalysts provide, have enabled access to a variety of new target motifs for synthesis, with extraordinary tolerance for heterocycles exhibited. Increased understanding of the catalytic mechanism and of the role of each reaction component have also led to additional applications of this mechanistic paradigm to new chemical transformations and total syntheses that otherwise would be unavailable or require more expensive and/or less sustainable catalysts.

