Efficient Control of \( \pi \)-Alkyne and Vinylidene Complex Pathways for the \( \text{W(CO)}_5 \) Catalyzed Synthesis of Two Types of Nitrogen-Containing Bicyclic Compounds


**Significance:** Reported is a tungsten-catalyzed regioselective synthesis of 3-azabicyclo[3.3.0]-octane and 2-azabicyclo[3.3.0]octane derivatives \( \text{C} \) and \( \text{D} \) from \( \pi \)-acetylenic dienol silyl ether \( \text{I} \). The reaction proceeds via different pathways \( \text{a} \) and \( \text{b} \) as a function of base. Thus, the initial vinylidene complex \( \text{A} \) undergoes double cyclizations and nitrogen facilitated 1,2-alkyl migration to lead to product \( \text{C} \). This mechanism is substantiated by \( ^{13} \text{C} \) as indicated and D-labeled experiments. In the absence of base, the tungsten-catalyzed process is envisaged to proceed via the zwitterionic intermediates \( \text{B} \) to lead to products \( \text{D} \). None of the intermediates were isolated.

**Comment:** The 2- and 3-azabicyclo[3.3.0]octane framework is found as part of bioactive molecules, for example in the inhibitor of DPP II (O. Danilova et al. *Bioorg. Med. Chem. Lett.* 2007, 17, 507). Traditionally, 3-azabicyclo[3.3.0]octane and 2-azabicyclo[3.3.0]octane derivatives are constructed respectively by reaction of dicarboxylic acid derivatives with amines (T. Punniyamurthy, T. Katsuki *Tetrahedron* 1999, 55, 9439) or intramolecular cyclization of 2-(2-bromoethyl)cyclopentamines (H. Booth et al. *J. Chem. Soc.* 1959, 1050). The present methodology constitutes a new catalytic route to both heterocyclic systems which proceeds in useful synthetic yields.