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Efficient Control of π-Alkyne and Vinylidene Complex Pathways for the W(CO)₅(L)-Catalyzed Synthesis of Two Types of Nitrogen-Containing Bicyclic Compounds

**W(CO)₅-Catalyzed Synthesis of 2- and 3-Azabicyclo[3.3.0]octanes**

**Significance:** Reported is a tungsten-catalyzed regioselective synthesis of 3-azobicyclo[3.3.0]octane and 2-azobicyclo[3.3.0]octane derivatives C and D from π-acetylenic dienol silyl ether 1. The reaction proceeds via different pathways a and b as a function of base. Thus, the initial vinylidene complex A undergoes double cyclizations and nitrogen facilitated 1,2-alkyl migration to lead to product C. This mechanism is substantiated by 13C as indicated and D-labeled experiments. In the absence of base, the tungsten-catalyzed process is envisaged to proceed via the zwitterionic intermediates B to lead to products 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-azobicyclo[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.