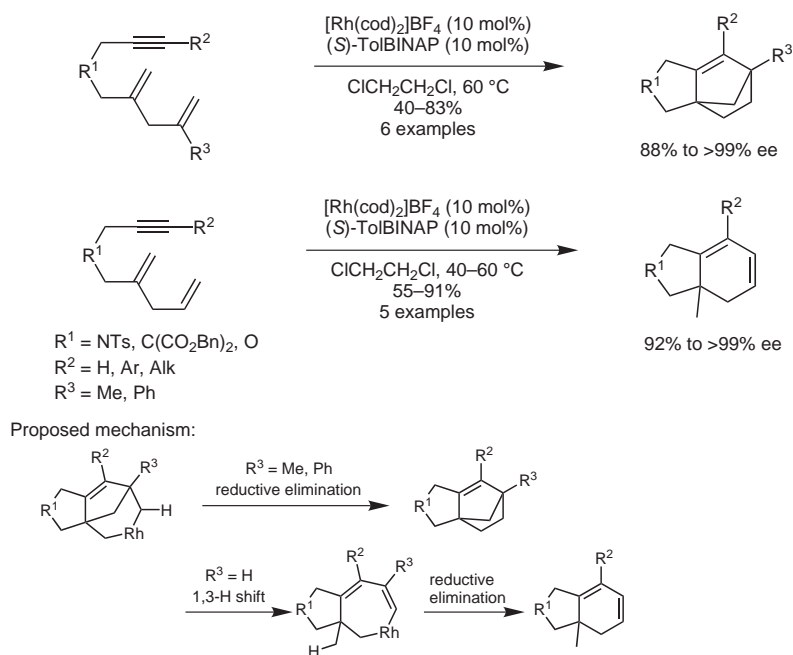


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Enantioselective Intramolecular [2+2+2] Cycloaddition of 1,4-Diene-yne: A New Approach to the Construction of Quaternary Carbon Stereocenters

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Chiral Quaternary Carbon Stereocenters via Diene-yne [2+2+2] Cycloaddition



Significance: In the presence of a [Rh(cod)₂]BF₄/Tol-BINAP catalyst system, diene-yne can be converted into either chiral substituted norbornenes or chiral bicyclic dienes in one step with excellent enantioselectivity and good to excellent yield. The key to the divergent product selectivity is the diene substituent R³, which is proposed to control the mechanism of the final bond-forming step. The reaction was also performed under an acetylene atmosphere, forming an allyl diene product in low yield.

Comment: Rhodium-catalyzed [2+2+2] cyclization reactions are novel methods for generating complex aromatic and alicyclic products (see review below). The method of Shibata and Tahara is particularly interesting, as the product can either be a strained alkene or a chiral diene, with one or more chiral quaternary carbon stereocenters. With regard to the diene product, the proposed mechanism includes a 1,3-H shift when R³ = H, allowing formation of a dienyrrhodium species which reductively eliminates to form the diene product; however, no isotopic labeling studies were performed to support this mechanism.

Review: S. Kotha, E. Brahmachary, K. Lahiri *Eur. J. Org. Chem.* **2005**, 4741-4767.

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