

Cascade Reaction of Camphor-Derived Diynes with Transition Metal Compounds

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Platinum(II) catalyzes the isomerization of camphor sulfonamide diynes in a cascade reaction involving annulation of a five-membered ring to the camphor skeleton, ring-enlargement by C-C bond cleavage, reduction of sulfur(VI) to sulfur(IV), and oxidation of a hydroxy group to a ketone. The reactions of the diynes with other transition metal compounds were also studied. Copper, gold and rhenium give final products similar to those obtained with simple Brønsted acids or halogens, mainly by annulation of a five-membered ring to the camphor moiety, accompanied by reduction of a sulfonamide to a sulfinamide group, but lacking the ring-enlargement step. Palladium(II) occupies an intermediate position as both types of products are obtained. The reaction mechanism and intermediates are discussed.