

Selective Reactions Based on Retro-allylation of Homoallyl Alcohols

Hideki Yorimitsu

(Dept. of Engineering, Kyoto Univ.)

Metal-mediated or -catalyzed retro-allylation of homoallyl alcohol has emerged as a new useful method for preparing allylmetals. The metal alkoxides of well-designed homoallyl alcohols undergo retro-allylation via chairlike six-membered transition states. Thanks to the conformationally rigid transition states, the retro-allylation reactions proceed regio- and stereospecifically, yielding regio- and stereochemically well-defined allylmetals. The allylmetals thus generated are used in situ, which can afford allylated products with high selectivity. Retro-allylation reactions mediated by zirconium, gallium, and palladium are described.

Retro-allylation of bulky gallium homoallylic alkoxides occurs to generate (*Z*)- and (*E*)-crotylgallium reagents stereospecifically, starting from *erythro*- and *threo*-homoallylic alcohols, respectively. The (*Z*)- and (*E*)-crotylgallium reagents immediately reacted with aromatic aldehydes to afford the corresponding *erythro*- and *threo*-homoallylic alcohols, respectively.

Treatment of tertiary homoallyl alcohol with aryl halide under palladium catalysis resulted in the transfer of the allyl moiety of the homoallyl alcohol to aryl halide and yielded the corresponding cross-coupling product stereo- and regioselectively. The transfer process includes retro-allylation, which proceeds via a conformationally regulated six-membered transition state. The retro-allylation can be regarded as a method for the stereo- and regioselective preparation of σ -allylpalladium.