

Theoretical investigation on the rhodium-catalyzed coupling reaction of ketoxime with 1,3-enynes: $[4 + 1]$ vs. $[4 + 2]$ annulation

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June 19, 2020

Abstract

The mechanisms of rhodium-catalyzed coupling reaction of ketoxime and 1,3-enynes were investigated by employing the density functional theory (DFT) calculations. Different 1,3-enynes would lead to different annulation products. Reaction A undergoes five sequential steps (C-H activation, 1,3-enyne migratory insertion, 1,4-Rh migration, cyclization, and deprotonation) to lead to $[4 + 1]$ annulation product. Whereas, due to the electronic effect, the process generating $[4 + 2]$ product in reaction A is restricted. In contrast, the electron-withdrawing group of N(Me)₂ group in 1,3-enyne would bring about the $[4 + 2]$ annulation product in reaction B. Our calculated results indicate that no $[4 + 1]$ annulation product could be obtained in reaction C, in agreement with the experimental observation that the cis-allyl hydrogen in 1,3-enyne is crucial for the $[4 + 1]$ annulation reaction.

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