

Stereoselective Synthesis of Seven-membered Carbocycles

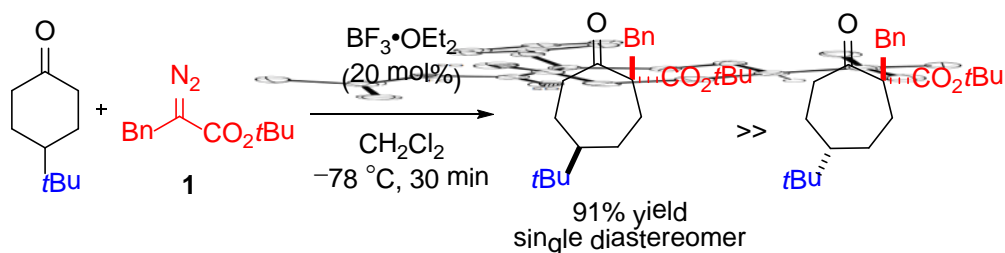
Using α -Alkyldiazoacetates

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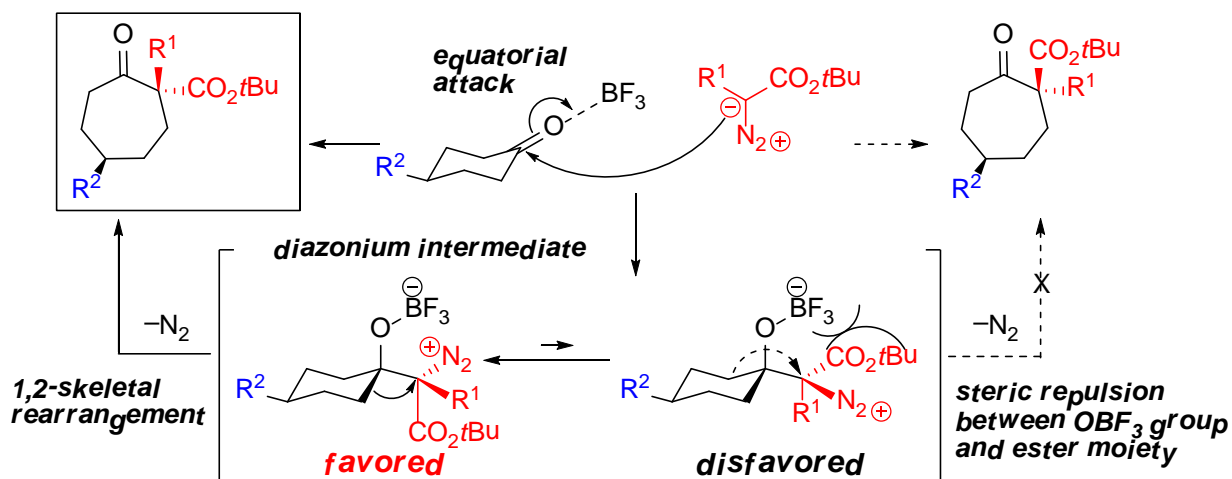
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Seven-membered carbocycles are carbon skeleton motifs found in various kinds of natural compounds, and some of these compounds have attracted attention due to their prominent biological activities. Therefore, the development of synthetic protocols for stereodefined seven-membered rings is one of the considerable issues in synthetic organic chemistry.

The ring expansion of readily available cyclohexanones would be considered as a method for facile construction of seven-membered carbocycles. In this context, I have investigated boron Lewis acid-catalyzed ring expansion of six-membered cyclohexanone derivatives with α -alkyldiazoacetates (**1**) to give the seven-membered rings with an all-carbon quaternary center.



Interestingly, the ring expansion of substituted cyclohexanones such as 4-*tert*-butylcyclohexanone gave the corresponding seven-membered rings having two remote stereogenic centers as a single diastereomer. I would like to talk about scope of the stereoselective ring expansion, plausible mechanism (*vide infra*) and development of catalytic enantioselective reaction.



ref: Hashimoto, T.; Naganawa, Y.; Maruoka, K. *J. Am. Chem. Soc.* **2009**, *131*, 6614.