

REGULAR ARTICLE

A DFT study on the reaction mechanisms of N-heterocyclic carbene catalyzed homodimerization of styrenes

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Abstract: In this study, the reaction mechanisms of selective tail-to-tail homodimerization of styrene catalyzed by N-heterocyclic carbene (NHC) have been firstly investigated using density functional theory (DFT). Four possible reaction channels (including the direct reaction channel and three NHC-catalyzed reaction channels) have been suggested and investigated in detail. Our calculated results indicate that one of the NHC-catalyzed channels is the most energetically favorable channel, which contains five reaction steps: the nucleophilic attack by NHC, DBU-assisted proton transfer, the dimerization, the direct [1,4]-proton transfer, and the regeneration of NHC. This work should be helpful for people to understand the dimerization at molecular level, and the novel DBU-assisted proton transfer process provides valuable insights on rational design of the suitable Brønsted acid/base catalysts for promoting this type of reaction.

AMS subject classifications: 92E99

Key words: DFT; Reaction mechanism; NHC; Homodimerization; DBU.

Introduction

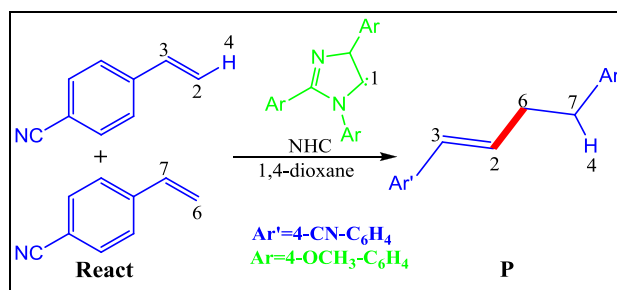
Homodimerization, which means the homocoupling reaction, usually provides new industrial raw materials and valuable productions with high selectivity and high speed

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manner under the catalytic condition, and thus has attracted more and more attention over the past decades [1-3]. For example, the homodimerizational reactions include the Wurtz-Fittig reaction, the Glaser reaction, the Ullmann reaction, the Cadiot-Chodkiewicz reaction, and so on [4-7]. Although the homodimerization has been widely applied in organic chemistry, the reaction generally requires the participation of the transition metal or ion catalyst and harsh conditions, so it is highly desired to develop the green and efficient method for this kind of reaction.

In recent years, the organocatalysis is being more and more widely used in this kind of homodimerizations, which is due to the distinguishing features of low-cost and environment-friendliness [8-10]. N-heterocyclic carbene (denoted as NHC), which is famous as one of the most powerful Lewis base organocatalysts, has been found to be an ideal choice for the organic reactions [11-13]. Noteworthy, Schedler and coworkers synthesized diaryl compounds by the homocoupling reactions between two same styrenes under NHC-catalyzed condition [14], and the reaction happens at 120 °C in 1,4-dioxane solvent with DBU as additives (depicted in **Scheme 1**). The reaction is very convenient and attractive, but its detailed mechanism remains unclear. There are still some questions that need to be solved: What are the possible mechanisms in detail? How does NHC catalyst work? What are the roles of NHC and the additive DBU? These questions and our research interests in the NHC catalysis promote us to perform a computational study not only for obtaining a preliminary picture for the homodimerization reaction mechanism, but also for exploring the special roles of NHC and additives. We believe that the computational results should be important for understanding the organocatalysis, and thus provides valuable insights on the rational design for this kind of reactions.

In the present work, the reaction between bimolecular reactant **React** (aryl styrene) catalyzed by catalyst **NHC** to generates product **P** (diaryl styrene, depicted in **Scheme 1**), was chosen as the research object of this theoretical investigation. The detailed reaction mechanisms were studied using the density functional theory, which had been widely used on the studies of the organic [15-31] and enzymatic [32] reaction mechanisms.



Scheme 1. The homodimerization of styrenes catalyzed by NHC