

A computational study on the mechanism for the GaCl₃-catalyzed [4 + 1] cycloaddition of α,β -unsaturated ketone and 2,6-dimethylphenyl isocyanide

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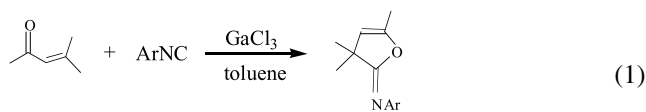
Abstract—The reaction of the GaCl₃-catalyzed [4 + 1] cycloaddition of α,β -unsaturated ketone with 2,6-dimethylphenyl isocyanide leading to unsaturated γ -lactone derivative has been investigated using the density functional theory with the B3LYP hybrid functional. According to our calculations we found that the reaction is stepwise and exothermic. The reaction proceeds via three steps. The first step is the coordination of GaCl₃ to the oxygen atom in mesityloxide leading to a more electrophilic C3 atom. At the second step, 2,6-dimethylphenyl isocyanide attacks mesityloxide to form the C3–C6 bond with GaCl₃ activator, which is the rate-limiting step. Finally, the C6–O bond is formed to give the five-member cycle product due to the attack of the C6 atom to the O atom. In addition, our calculations also suggest that GaCl₃ activator can be easily detached from the product. The theoretical results are in good agreement with the recent experimental observations. © 2004 Elsevier Ltd. All rights reserved.

1. Introduction

Isocyanides are stable organic compounds with an extraordinary functional group and a formally divalent carbon atom. This unusual valence structure and reactivity have been discussed for over one and a half centuries. One of the classic themes in the chemistry of isocyanides is related to the heterocycle synthesis. The synthetically most important property of isocyanides is the reaction with nucleophiles and electrophiles at the isocyanide carbon atom. Most of other functional groups in organic chemistry could react with nucleophiles and electrophiles at different centers. Therefore, isocyanides are usually recognized as useful building blocks in organic synthesis^{1,2} and in polymer science.³ Isocyanides were widely used in cycloaddition reactions in the presence of promoters such as acids, Lewis acids, or transition metal complex. Ito and Saegusa⁴ reported that Et₂AlCl can promote 1,4-cycloaddition of α,β -unsaturated carbonyl compounds with isocyanides to afford unsaturated *N*-substituted iminolactones, which are stereoselectively converted to γ -butyrolactones via hydrogenation on Pd/C and then acid hydrolysis. Recently, GaCl₃ was used as a good activator in many organic reactions.^{5–11} Chatani and

co-workers¹² reported that GaCl₃ can promote the cycloaddition of α,β -unsaturated carbonyl compounds with isocyanides leading to unsaturated γ -lactone derivatives.

To our best knowledge, there are rare theoretical studies on the mechanisms of the GaCl₃-catalyzed reactions.^{13,14} In our previous calculations,¹³ we have showed that the GaCl₃ activator has high catalytic activity for the skeletal reorganization of enynes to 1-vinylcycloalkenes and the reaction undergoes a stereoselective reorganization. The motive of the present study is to clarify the mechanism of the GaCl₃-catalyzed [4 + 1] cycloaddition of α,β -unsaturated ketone with 2,6-dimethylphenyl isocyanide leading to unsaturated γ -lactone derivative (Eq. 1) and to make clear that GaCl₃ is desirable for the detachment from the product. To this end, we have performed detailed calculations using the B3LYP hybrid functional method to study the title reaction mechanism. In addition, we have carried out the natural bond orbital (NBO) analysis to observe the bond order changes in the process of the reaction.

Ar = 2,6-Me₂C₆H₃

Keywords: GaCl₃; DFT; Cycloaddition; α,β -Unsaturated ketone; Isocyanides.

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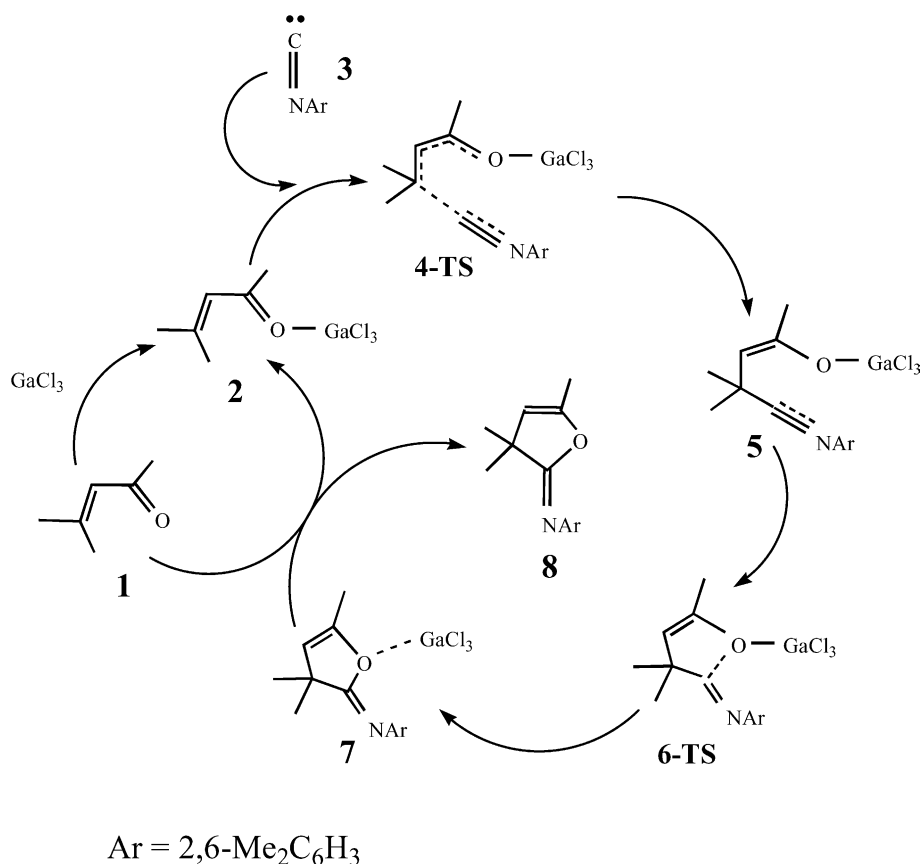


Figure 1. Catalytic cycle for the title reaction.

2. Computational details

All calculations were carried out with the Gaussian 98 program.¹⁵ The structures of all the reactants, transition states, intermediates, and products were located and characterized with the DFT calculations using the B3LYP hybrid functional.^{16,17} The 6-31G* basis set for all atoms were used to optimize this series of relevant structures. For all stationary points, vibrational frequencies were also calculated to investigate the nature of the stationary points and to provide the thermodynamic quantities such as the zero-point vibrational energies (ZPVE), thermal corrections, enthalpies, Gibbs free energies and entropies at the temperature of 298.15 K and the pressure of 1 atm. Each stationary point was characterized as a minimum with all positive frequencies and a transition state with only one imaginary frequency. Single-point energies were further calculated at the B3LYP/6-311++G** level. In order to take into account the solvent effect, we also adopt the self-consistent reaction field (SCRF) method based on the polarized continuum model (PCM)¹⁸ for the title reaction. In addition, the electronic structures of all stationary points were analyzed by the natural bond orbital (NBO) method.¹⁹

3. Results and discussions

In this work, as shown in Figure 1, we have explored the catalytic cycle for the title reaction. The corresponding

geometries and parameters are listed in Figure 2 and Table 1, respectively.

3.1. The process of the title reaction with GaCl₃ activator

As shown in Figure 2 and Table 1, there exist two transition states in the title reaction. According to the calculational results, the whole reaction process is found to be proceeded via three steps as follows.

3.1.1. First step—formation of the complex 2. The first step is the coordination of GaCl₃ to the lone pair electrons of the O atom in mesityloxide **1**. At the B3LYP/6-31G* level, the C1=O and C2=C3 bond lengths were found to be 1.2634 and 1.3650 Å in **2**, which are about 0.04 and 0.015 Å longer than those in **1**, while the C1–C2 bond length is 1.4425 Å in **2**, which is about 0.04 Å shorter than that in **1**. Wiberg bond indices given in Table 3 show that the bond orders of the C1=O and C2=C3 bonds change from 1.7506 and 1.7718 in **1** to 1.4451 and 1.6561 in **2**, respectively, while the bond order of the C1–C2 bond changes from 1.0722 in **1** to 1.1912 in **2**. The natural charge of C3 atom changes from 0.096 in **1** to 0.176 in **2** with natural population analysis (NPA). Therefore, the coordination of GaCl₃ to the oxygen atom in **1** results in the weakness of the C1=O and C2=C3 bonds and the enhancement of the C1–C2 bond, leading to a more electrophilic C3 atom. As shown in Table 2, the binding energy is 32.98 kcal/mol (including ZPVE) at 25 °C at the B3LYP/6-31G* level and 25.53 kcal/mol without ZPVE at the B3LYP/6-311++G**

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