Zn(II)-catalyzed Rearrangement of Epoxides Using an Ionic Liquid

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The opening of epoxide rings catalyzed by Zn(II) has been studied by many scientists since it is the first step in the carboxylation of epoxides to carbonates. Several catalytic systems, such as Bronsted or Lewis acids, lithium salts, MgBr₂·Et₂O, or [DDMIm]I, have been developed for the rearrangement of epoxides to carbon compounds. However, there has been little success in the selective rearrangement of epoxides by the formation of by-products and low yield.

In studying the rearrangement of sterically hindered epoxides, we have found that in the absence of carbon dioxide, these epoxides rearranges to carbon compounds. For example, trans-stilbene oxide is rearranged to deoxybenzoin selectively, while cis-stilbene oxide is not reactive under our reaction conditions. Since there has been no report using Zn(II) with ionic liquid for the rearrangement of epoxides, our system seems to be quite interesting in two aspects: (1) Only one isomer, trans-stilbene oxide, is reactive under our reaction conditions. (2) Only one rearrangement product, deoxybenzoin, is obtained selectively.

In this paper, we report our results on the use of imidazolium-based ionic liquids with Zn(II) for the rearrangement of epoxides as well as theoretical investigation of these reactions.

1-Decyl-2,3-dimethylimidazolium iodide ([DDMIm]I) was prepared by reacting methyl iodide with 1-decyl-2,3-dimethylimidazole. Trans- and cis-stilbene oxides were prepared by reacting corresponding stilbene with m-CPBA under N₂ in dichloromethane. After workup with NaHCO₃ and further purification with column chromatography, the product was obtained as a pure solid. Rearrangement reaction was carried out by contacting stilbene oxide with [DDMIm]I and ZnCl₂ in 10 mL of N-methylpyrrolidinone (NMP) in a high-pressure stainless steel bomb reactor. The reaction proceeded cleanly without producing any side product except where it was noted in the Table 1. Typical side products of the product were identified as diphenylacetaldehyde and benzophenone by NMR and GC-MSD analysis. These are known to be produced via uncatalyzed thermal radical process.

[DDMIm]I was chosen as an ionic liquid for the reaction since it was most stable under our reaction conditions among various ionic liquid we tested. Table 1 shows the results of the rearrangement of stilbene oxide catalyzed by Zn(II) and ionic liquid [DDMIm]I.

The yield increased as the increase of the reaction time (entry 1-3). Without [DDMIm]I and Zn(II), the reaction was very slow also producing side products (entry 4). With [DDMIm]I alone the reaction was still slow (entry 5). Only with the co-presence of both Zn(II) and [DDMIm]I, the reaction goes to completion (entry 7). The reaction rate is strongly dependent on the concentrations of Zn(II) (entry 6, 7) and [DDMIm]I (entry 7, 8 or entry 6, 9).

Rearrangements of other epoxides were also studied and shown in Table 2. Trans-stilbene oxide was found to rearrange to deoxybenzoin, whereas cis-stilbene oxide was not under the same reaction condition (entry 1-2). The reaction rate increased significantly when a phenyl group of stilbene oxide was replaced by a methyl group (entry 3). The reaction rate was accelerated further when both phenyl groups were substituted by methyl groups, resulting in conversion of 2,3-dimethyl oxirane even at 80 °C (entry 4) where trans-stilbene oxide is unreactive (entry 5).

The stability of Zn(II) complexes with stilbene oxides and...
their reaction with iodide ion followed by rearrangement were theoretically investigated at the BP86 level of the theory (TZP/DZP basis) using Amsterdam Density Functional (ADF) program. The optimized structures of cis-stilbene oxide (1), trans-stilbene oxide (2) and ZnI2 (3) are shown in Figure 1. Energetically cis- and trans-stilbene oxides are almost same. When epoxide ring is opened by the attack of the iodide ion assisted by coordination of oxygen to Lewis acidic Zn(II), cis-stilbene oxide complex (4) becomes less stable than trans-stilbene oxide complex (5) by 3.5 kcal/mol because two phenyl rings are now in gauche conformation (Figure 2). The intermediate 5 is calculated to be more stable than the reactants 1 and 3 by 7.9 kcal/mol, because of the release of the ring strain and the stabilization the negative charge on the oxygen by coordination to Zn(II). For the rearrangement reaction to take place, 60° rotation around C-C bond should occur. In case of cis-stilbene oxide this rotation puts two phenyl groups in eclipsed conformation. This might be the main reason for the inactivity of cis-stilbene oxide toward rearrangement under our reaction condition. For the trans-stilbene oxide complex, the removal of hydrogen iodide seems to be the rate-limiting step with the activation energy of 11.7 kcal/mol. This removal process is assisted by the another iodide ion coordinated to Zn(II) as shown in the structure of the transition state (6) in Figure 3. In the transition state, the iodide ion is almost completely dissociated, while the proton is still close by possibly interacting with the developing C-C double bond. As a whole, the reaction is calculated to be exothermic by 21.9 kcal/mol.
In conclusion, we were able to selectively rearrange trans-stilbene oxide to deoxybenzoin using Zn(II) and ionic liquid as a catalyst under relatively mild reaction condition and using computational method we proposed the plausible mechanism for the reaction.

Computational Details

Stationary points on the potential energy surface were calculated using the Amsterdam Density Functional (ADF) program, developed by Baerends et al.\(^6\) and vectorized by Ravenek.\(^7\) The numerical integration scheme applied for the calculations was developed by te Velde et al.\(^8\) The geometry optimization procedure was based on the method due to Versluis and Ziegler.\(^9\) The electronic configurations of the molecular systems were described by double-\(\zeta\) STO basis sets with polarization functions for the H, C and O atoms, while triple-\(\zeta\) Slater type basis sets were employed for the I and Zn atoms.\(^10\) \(1s\rightarrow 4p\) electrons of I, and the \(1s\rightarrow 2p\) electrons of Zn were treated as frozen cores. A set of auxiliary \(s, p, d, f\) and \(g\) STO functions, centered on all nuclei, was used in order to fit the molecular density and the Coulomb and exchange potentials in each SCF cycle. Energy differences were calculated by augmenting the local exchange-correlation potential by Vosko et al.\(^6\) with Becke's\(^4\) nonlocal exchange corrections and Perdew's\(^5\) nonlocal correlation corrections (BP86). Geometries were optimized including nonlocal corrections at this level of theory. First-order Pauli scalar relativistic corrections\(^22,23\) were added variationally to the total energy for all systems. In view of the fact that all systems investigated in this work show a large HOMO-LUMO gap, a spin-restricted formalism was used for all calculations. No symmetry constraints were used.

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References