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.[1] Several catalytic systems, such as Brønsted or Lewis acids,[2] lithium salts,[3] $MgBr_2$,[4] Pd complex,[5] $InCl_3$,[6] $IrCl_3 \cdot nH_2O$,[7] $Er(OTf)_3$,[8] $Sn(OTF)_2$[9] or $BiOClO_4$,[10] have been developed for the rearrangement of epoxides to carbonyl compounds. However, there has been little success in the selective rearrangement of epoxides, being plagued by the formation of byproducts and low yield.

In studying the carboxylation of sterically hindered epoxides, we have found that in the absence of carbon dioxide these epoxides rearranges to carbonyl 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.
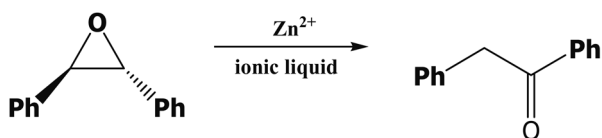
In this paper, we report our results on the use of imidazolium-based ionic liquids with Zn(II) for the rearrangement of epoxides as well as theoretical investigation of these reactions.

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 N_2 in dichloromethane. After workup with $NaHCO_3$ 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 ZnI_2 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 diphenyl

Table 1. Rearrangement of *trans*-stilbene oxide in NMP at 120 °C

entry	*trans*-stilbene oxide (mmol)	[DDMIm]I (mmol)	ZnI_2 (mmol)	reaction time (h)	yield (%)[a]
1	19.0	1.25	0.03	6	10
2	19.0	1.25	0.03	15	48
3	19.0	1.25	0.03	24	60
4	19.0	0	0	15	7.1(6.0)[b]
5	19.0	1.25	0	15	17(14)[b]
6	9.5	1.25	0.03	15	67
7	9.5	1.25	0.06	15	100
8	9.5	0.625	0.06	15	40
9	9.5	1.875	0.03	15	91

[a]The yields were determined by NMR based on the area ratio between the product and the reactant since there is no other species present. [b]Side products were produced. The yield of the side products is shown in the parenthesis.

acetaldehyde 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).
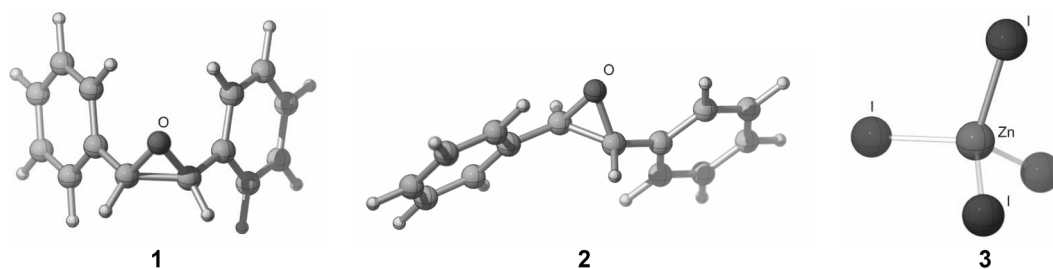
The stability of Zn(II) complexes with stilbene oxides and

Figure 1. Optimized structures of reactants.

Table 2. Rearrangement of other epoxides in NMP[a]

entry	epoxide	temperature (°C)	reaction time (h)	yield (%)
1	*cis*-stilbene oxide	120	15	0
2	*trans*-stilbene oxide	120	15	67
3	2-methyl-3-phenyl oxirane	120	15	98
4	2,3-dimethyl oxirane	80	24	25
5	*trans*-stilbene oxide	80	120	0

[a]Epoxide 9.5 mmol, [DDMIm]I 1.25 mmol, and ZnI$_2$ 0.03 mmol

Figure 3. Optimized structure of the transition state.

Figure 2. Optimized structures of the intermediates after ring opening.
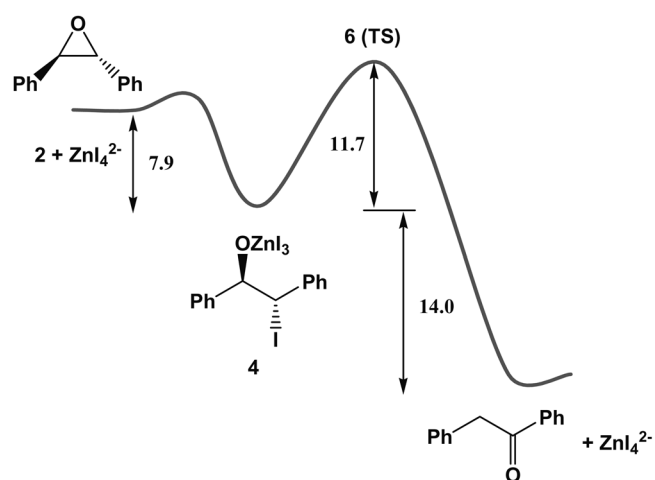
Figure 4. Potential energy surface for the rearrangement reaction. Energies in kcal/mol.

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 ZnI$_4^{2-}$ (**3**) are shown in Figure 1. Energetically *cis*- and *trans*-stibene 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
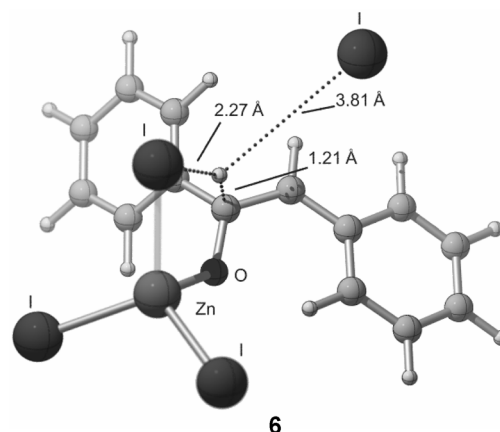
rotation puts two phenyl groups in eclipsed conformation. This might be the main reason for the inactivity of *cis*-stilbene oxide toward rearrangement under our reaction condition. For the *trans*-stilbene oxide complex, the removal of hydrogen iodide seems to be the rate-limiting step with the activation 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.*[11,12] and vectorized by Ravenek.[13] The numerical integration scheme applied for the calculations was developed by te Velde *et al.*[14,15] The geometry optimization procedure was based on the method due to Versluis and Ziegler.[16] The electronic configurations of the molecular systems were described by double-ζ STO basis sets with polarization functions for the H, C and O atoms, while triple-ζ Slater type basis sets were employed for the I and Zn atoms.[17,18] The 1s electrons of C and O, the 1s-4p electrons of I, and the 1s-2p electrons of Zn were treated as frozen cores. A set of auxiliary[19] 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.*[20] with Becke's[21] nonlocal exchange corrections and Perdew's[22] nonlocal correlation corrections (BP86). Geometries were optimized including nonlocal corrections at this level of theory. First-order Pauli scalar relativistic corrections[23,24] 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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