

## 理論計算を用いたシクロアルキン類とエチレン類の

## [2+2]環化付加反応機構の解明

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**Abstract :** In this paper, concerted [2+1] path and biradical path have been investigated for reaction of small-ring cycloalkynes with ethylenes. No one has consistently succeeded to clarify experimental results theoretically yet. In this work, we use long-range corrected (LC) density functional,  $\omega$ B97X-D, and (U)CCSD(T) to describe experimental results. As compared with the previous report of B3LYP (no LC), we found LC plays an important role for reproducing [2+2] cycloadditions.

Cyclopentyne (**1**) reacts with monoenes to form [2+2]cycloadducts with complete retention of stereochemistry<sup>1,2</sup> (Scheme 1) and benzyne (**2**) reacts with monoenes similarly, but with partial loss of stereochemistry<sup>3</sup> (scheme 2). Conrotatory [2+2] cycloadditions are thermally forbidden by the Woodward-Hoffman rules, hence biradical path and concerted [2+1] path have been proposed alternatively (Scheme 3). Biradical path will lose stereochemistry because C-C bond in ethylene moiety of **b** will rotate. In contrast, concerted [2+1] path retains stereochemistry.

As compared with the experimental results, **1** should prefer concerted [2+1] path and **2** should prefer biradical path. To the best of our knowledge, no one have calculated the [2+2] cycloaddition of both **1** and **2** except for Kinal<sup>4,5</sup> et al. According to their reports, the CCSD(T) method and the B3LYP method fail to explain complete retention of stereochemistry for the reaction of **1**. Hence, we performed further computational study on the two paths.

We adopted the unrestricted CCSD(T) method and the  $\omega$ B97XD method, which is density functional with long-range correction and dispersion correction. For the reaction of **1**, the (U)CCSD(T) calculations and the  $\omega$ B97XD calculations prefer [2+1] path to biradical path kinetically by 4.1 and 3.3 kcal/mol, respectively. These values are large enough to explain complete retention of stereochemistry. For the reaction of **2**, the (U)CCSD(T) calculations prefer [2+1] path kinetically and prefer biradical path thermodynamically, which give rise to partial loss of stereochemistry. In other words, kinetic factors and thermodynamic factors compete against each other.

- (1) Fitjer, L.; Modarelli, S. *Tetrahedron Lett.* **1983**, *24*, 5495–5498.
- (2) Gilbert, J.; Baze, M. *J. Am. Chem. Soc.* **1984**, *106*, 1885–1886.
- (3) Jr, M. J.; Levin, R. *J. Am. Chem. Soc.* **1969**, *91*, 6411–6415.
- (4) Ozkan, I.; Kinal, A. *J. Org. Chem.* **2004**, *69*, 5390–5394.
- (5) Kinal, A.; Piecuch, P. *J. Phys. Chem. A.* **2006**, *110*, 367–78.

