C₆₀ as a Chemical Probe : Photolysis and Thermolysis of Diazirines with C₆₀

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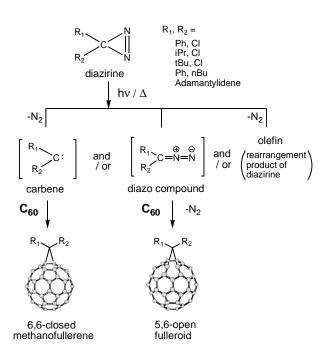
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Photolysis and thermolysis of diazirines have been widely used to produce carbenes.¹ And, diazirines have recently been acted as photoaffinity reagents to investigate the organization in the area of biological chemistry.² Presently, three elementary processes are known in the photolysis of diazirines, the production of carbene, the production of a diazo compound, and the rearrangement in the exited state (RIES) of diazirine.³ On the other hand, it has been reported that C_{60} fullerene reacts with carbene to yield methanofullerene and with diazomethane to fulleroid.⁴ These differences might be useful in differenciating whether carbene or diazo compound is involved as the reactive intermediate. In the context, we have carried out the photolysis and the thermolysis of several diazirines in the presence of C_{60} . We also performed calculations on the energetics of the thermolysis of diazirnes.

Our study indicated that C_{60} can be used as a probe to distinguish carbene and diazo compound during the photolysis and the thermolysis of diazirines by determing the isomeric ratio of the formed methanofullerene and fulleroid.⁵ This C_{60} probe method can show not only the partitioning of carbene/diazo, but also the rearrangement process of diazirines.



References

- Chemistry of Diazirines; Liu, M. T. H., Ed., Florida, 1987; Vols 1 & 2.
- (a) Richards, F. M.; Lamed, R.; Wynn, R. Protein Science, 2000, 9, 2506-2517; (b) Korshunova, G. A.; Sumbatyan, N. V.; Topin, A. N. Mol. Biol., 2000, 34, 823.
- (a) Platz, M. S. In: *Carbene Chemistry*; Bertrand, G., Ed.; Marcel Dekker Inc.: New York, 2002, p27-174.
 (b) Merrer, D. C.; Moss, R. A. In: *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; Elsevier: Amsterdam, 2001, Vol 3, p53-113.
- 4. For reviews, see: (a) *Fullerenes and Related Structures*, Hirsh, A., Ed.; Springer: Berlin, 1999; (b) Diederich, F.; Isaaca, L.; Philip, D. *Chem. Soc. Rev.* **1994**, 243.
- (a) Akasaka, T.; Liu, M. T. H.; Niino, Y.; Maeda, Y.; Wakahara, T.; Okamura, M.; Kobayashi, K.; Nagase, S. J. Am. Chem. Soc. 2000, 122, 7134-7135; (b) Wakahara, T.; Niino, Y.; Kato, T.; Maeda, Y.; Akasaka, T.; Liu, M. T. H.; Kobayashi, K.; Nagase, S. J. Am. Chem. Soc. 2002, 124, 9465-9468; (c) Liu, M. T. H.; Choe, Y-K.; Kimura, M.; Kobayashi, K.; Nagase, S.; Wakahara, T.; Niino, Y.; Ishitsuka, M. O.; Maeda, Y.; Akasaka, T. J. Org. Chem. 2003, 68, 7471-7478.