Diastereoselective Intramolecular (3+2) Cycloadditions of Epoxy & Aziridinyl Enolsilanes

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We have been studying and exploiting the reactivity of epoxy and aziridinyl enolsilanes for inter- and intramolecular (4+3) cycloadditions with dienes such as cyclopentadiene and furan, to produce cycloheptanoid cycloadducts in high yields and with good diastereo- and enantiomeric excesses.[1]

When we used open dienes in intramolecular reactions with aziridinyl enolsilanes or epoxy enolsilanes, diastereoselective (3+2) cycloadditions occurred instead to afford perhydroindanes bearing four contiguous stereocenters. These cycloadditions proceed by a stepwise mechanism, through an activated epoxide or aziridine 4 as intermediate. When the reaction was carried out with enantiomerically pure aziridines (Eq. 1) and epoxides (Eq. 2), cycloadducts were obtained with retention of *ee*. This reaction could be applicable as a key step in the asymmetric total synthesis of natural products such as (–)-oplopanone.

[1] (a) Chung, W. K.; Lam, S. K.; Lo, B.; Liu, L. L.; Wong, W.-T., Chiu, P. *J. Am. Chem. Soc.* **2009**, *131*, 4556; (b) Krenske, E. H.; Lam, S.; Ng, J. P. L.; Lo, B.; Lam, S. K.; Chiu, P.; Houk, K. N. *Angew. Chem. Int. Ed.* **2015**, *54*, 7422.