新規ドミノ反応を用いる光学活性シクロヘキセン誘導体の立体選択的合成

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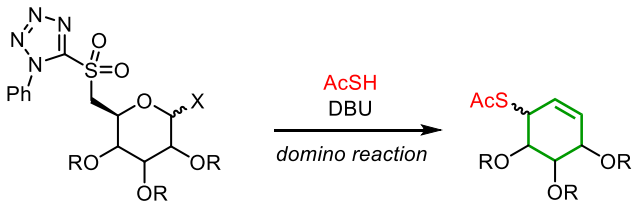
Stereoselective synthesis of optically active cyclohexene derivatives using a novel domino reaction ([1]*Faculty of Engineering, Gifu University* [2]*G-CHAIN, Gifu University,* [3]*iGCORE, Gifu University*) ○Wakaba Arai,[1] Natsuhisa Oka,[1,2,3] Kei Sugiura,[1] Minami Furuzawa,[1] Mayuka Kanda,[1] Kaori Ando[1]

Optically active cyclohexene derivatives are useful as synthetic intermediates for biologically active natural products, and the development of efficient synthetic methods for these compounds is of particular importance. We have found that hexose-derived Julia-Kocienski sulfones having a leaving group and a heteroarylsulfonyl group at the 1- and 6-positions, respectively, afford cyclohexene derivatives having an acetylthio group by treatment with DBU in the presence of thioacetic acid (Scheme 1). This transformation is considered to be a novel domino reaction consisting of the α-deprotonation of the heteroaryl sulfone, the elimination of the leaving group and the generation of an α,β-unsaturated sulfone, the Michael addition of thioacetic acid to the α,β-unsaturated sulfone, followed by an intramolecular Julia-Kocienski reaction. Cyclohexenes were obtained in modest to good yields with high *cis*-selectivity.

Keywords : Domino reaction; Cyclohexene; Sugar; Julia-Kocienski reaction; Stereoselective

光学活性シクロヘキセン誘導体は生物活性天然物の合成中間体などとして有用であり、効率的な合成法の開発は重要な課題である。我々は、グルコースやマンノースなどのヘキソースの 1 位に脱離基、6 位にヘテロアリールスルホニル基をもつ Julia-Kocienski スルホン **1** を合成し、チオ酢酸の存在下 DBU と反応させると、アセチルチオ基が導入されたシクロヘキセン **2** が、中程度から良好な収率、高い *cis* 選択性で得られることを見出した（Scheme 1）。これは、スルホン α 位の脱プロトン化、1 位脱離基の脱離と α,β-不飽和スルホンの生成、チオ酢酸の Michael 付加、分子内 Julia-Kocienski 反応からなるドミノ反応を経由したと考えられる。



1 **2**

Scheme 1. One-step synthesis of cyclohexene derivatives **2** from Julia-Kocienski reagents **1**.