硫黄官能基を持つ Weiss ジケトンの合成とその位置特異的変換

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The synthesis of the Weiss diketone bearing sulfide groups and its regiospecific transformation

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Weiss diketone bearing a bicyclo[3.3.0]octane skeleton has played a pivotal role as a versatile intermediate for natural products and ligands owing to its characteristic ring-fused structure and facile synthetic access. However, regioselective transformations of Weiss diketone, such as the functionalization of α -carbon of carbonyl moieties and transformations via enolization, remain challenging despite the potential synthetic utility. To address this issue, we have established a synthetic method of a Weiss diketone derivative 1 bearing four phenylthio groups, which allows further regiospecific functionalizations. In this presentation, the structural features of intermediate 1 and the details of its reactivity will be discussed.

Keywords: Weiss diketone; sulfur; regiospecific transformation

ビシクロ [3.3.0] 骨格をもつ Weiss ジケトンは,縮環 5 員環骨格と入手容易性に起因して天然物や配位子の合成中間体として重宝されている[1]. Weiss ジケトンを位置選択的に変換できれば,その合成化学的な価値は一層高まると期待される. しかし,高い対称性に起因して,Weiss ジケトンの位置選択的な官能基化,特にケトンの α 位の官能基化とエノール化を経る反応は困難である. 今回我々は,Weiss ジケトン骨格の位置特異的な変換法の確立に取り組んだ結果,Weiss ジケトンに硫黄求電子剤を作用させることで,対角の α 位がフェニルチオ基で完全に置換された化合物 α を得ることに成功した. この α を用いることで,Weiss ジケトン骨格に種々の官能基を位置選択的に導入できることを明らかにした.

[1] Fu, X.; Cook, J. M. Aldrichimica Acta 1992, 25, 43.