

テトラアザ型ジベンゾクリセンの合成開発

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Synthesis of a cardo-typed bisphenol fused with a dibenzo[*g,p*]chrysene

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A three-step synthesis of hexa-cycle fused-ring wherein two phenanthroline frameworks are pseudo-merged, namely [1,10]phenanthrolino[5,6-*f*][1,10]phenanthroline, was investigated. From a retro-synthetic point of view, the commercially available 4,5-diaza-9-fluorenone was used as a starting material: we expected that homo-dimerization of the fluorenone might afford the corresponding spiroketone, and the following reduction and acid-mediated migration could yield the target six-ring fused-heterocycle. In real synthetic approach, unlike prior dimerization of hydrocarbon fluorenones, the labile intermediate of the corresponding penta-oxy-phosphorane was isolated. The phosphorane sparingly underwent the desired rearrangement, yielding the spiroketone.

Keywords : Polyaromatic heterocycles; Dibenzo[*g,p*]chrysene; Fluorenone; Homo-dimerization; Tetradentate nitrogen ligand

ジベンゾクリセンのベイ領域にある四つの炭素原子を全て窒素原子に置き換えた四座型の六環性複素環 ([1,10]フェナンスロリノ[5,6-*f*][1,10]フェナンスロリン) の合成に挑戦した。計画した合成経路は、市販の 4,5-ジアザフルオレノン を二量化してスピロケトンへ誘導し、続く還元反応によるスピロアルコールへの変換とカチオン転位反応による芳香環化を経て、目的縮環体へつながるスキームである (Figure 1)。実際に 4,5-ジアザフルオレノンの二量化反応に取り組んだところ、従前の炭化水素のフルオレノンを用いた場合と同じようには円滑に進行しなかった。一方、合成中間体であるペンタオキシホスホランが単離され、対応するスピロケトン合成がかろうじて達成された。

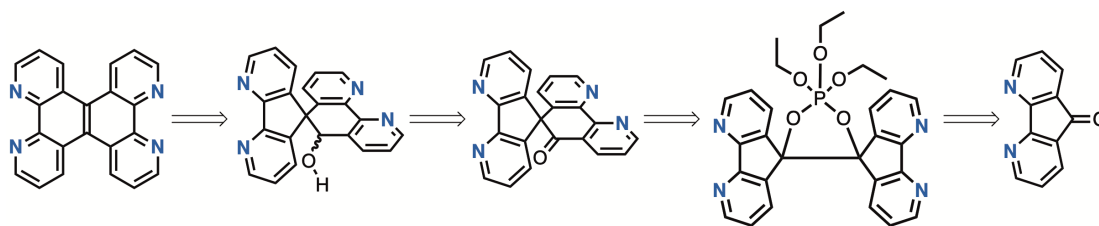


Figure 1. Retrosynthetic approach to an artificial tetradentate nitrogen ligand, namely [1,10]phenanthrolino[5,6-*f*][1,10]phenanthroline, in which commercially available 4,5-diaza-9-fluorenone might work as a significant starting material.

1) Y. Fujii, Y. Taguchi, S. Tokai, Y. Matsumoto, N. Yoshida, T. Iwasawa, *Tetrahedron* **2021**, 95, 132353. “Relevant Analysis to the Productivity in Selective Synthesis of Dibenzo[*g,p*]chrysene Derivatives” Doi: 10.1016/j.tet.2021.132353