Development of Environmentally Benign Julia Olefination by Reductive Desulfonylation Utilizing Pyrene Photocatalyst

(*Okayama University of Science*) ○Hikaru Watanabe, Kazuki Nakajima, Ryota Edagawa, Yasuhiro Okuda, Akihiro Orita

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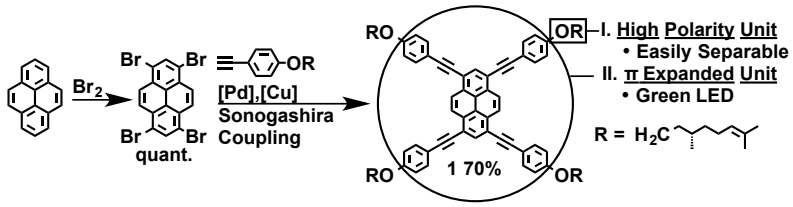
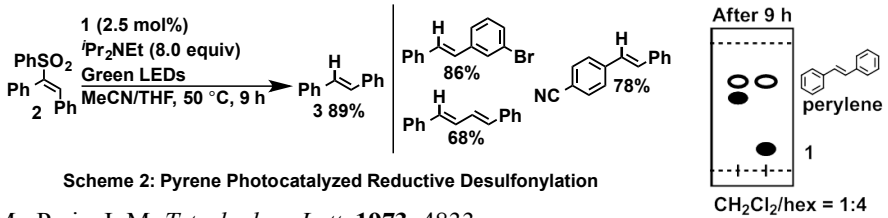
Julia olefination is widely used in synthesis of carbon–carbon double bonds starting from sulfones and aldehydes. Although this protocol is useful due to its mild reaction conditions and high *E*-selectivity, a use of toxic Na(Hg) is required for reductive desulfonylation of *β*-acetoxy sulfone intermediates.[1]

Recently we reported perylene photocatalyst-promoted reductive desulfonylation of ethenyl sulfones which were derived from *β*-acetoxy sulfones. Although this alternative Julia olefination worked well in desulfonylation of various ethenyl sulfones, it was often difficult to separate the perylene photocatalyst from olefinic products due to a small difference of their polarities. To overcome this drawback, we developed easily separable photocatalyst **1** for desulfonylation. The photocatalyst **1** was easily synthesized from pyrene via consecutive tetrabromination and Sonogashira coupling. Pyrene **1** was composed of two components: (I) branched long alkoxy groups and (II) highly expanded π-system. The former could assist high solubility and easy separation of **1** from the desired olefinic products, and the latter could enable lower energy of visible light to promote a catalytic system (Scheme 1).



Scheme 1: Synthesis of Pyrene Photocatalyst

When visible light (green LEDs) was irradiated at an MeCN/THF solution of ethenyl sulfone **2**, **1**, and *i*-Pr_2NEt, the desired reductive desulfonylation proceeded in 9 h, and **3** was successfully purified by column chromatography (Scheme 2). We also synthesized olefins functionalized by bromo, cyano, and dienyl groups.



Scheme 2: Pyrene Photocatalyzed Reductive Desulfonylation

1) Julia, M.; Paris, J. M. *Tetrahedron Lett.* **1973**. 4833.

2) Watanabe, H.; Takemoto, M.; Adachi, K.; Okuda, Y.; Dakegata, A.; Fukuyama, T.; Ryu, I.; Wakamatsu, K.; Orita,A. *Chem. Lett.*, **2020**, *49*, 409.