Wavelength-dependent formation of cycloreversion products from thietanes

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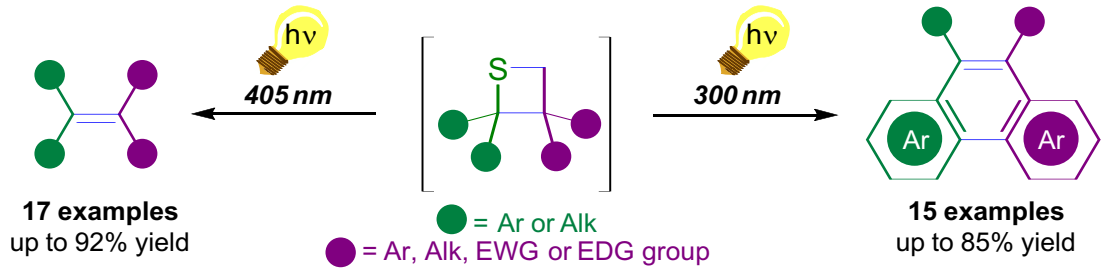
Because of their ubiquitous nature, alkenes have been the subject of extensive research and the olefin metathesis reaction rapidly supplanted the Wittig olefination to become the method of choice for preparing them. More recently, metal-catalyzed and photochemical carbonyl-olefin metathesis reactions, including the formation of the oxetane ring followed by the cycloreversion of the strained ring, emerged as reliable alternative strategies.[1-2] A Mallory electrocyclization reaction could also be included in the process to achieve functionalized phenanthrene derivatives.[3]

In contrast to oxetanes, fragmentation of thietanes,[4] which are their sulfur analogs, has been way less explored to date due to their synthetic access, which remained challenging until recently. Indeed, our group newly reported a domino photochemical synthesis of a wide variety of thietanes, where unstable thiocarbonyls are generated *in situ* via a Norrish-type II fragmentation of phenacyl[5] or pyrenacyl[6] sulfide precursors, which then participate in a thia-Paternò–Büchi reaction with diverse alkene partners.

Taking advantage of the straightforward access to functionalized thietanes, we investigated the cycloreversion of these four-membered ring sulfur-containing heterocycles and developed a selective general synthesis of sterically-hindered alkenes or phenanthrenes by a simple adjustment of the wavelength of irradiation of thietane substrates.



References

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