Photochemical Iodine Atom Transfer Radical Addition & Cyclization for the Synthesis of Organoboron Derivatives, Cyclopropanes and Cyclopentanes

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The last 20 years, organic synthetic photochemistry, an alternative green and sustainable approach, has experienced a renaissance paving the way for the discovery of novel reactivities[1]. Atom Transfer Radical Addition (ATRA), is one of the most common photochemical reactions, pioneered by Kharasch developing numerous examples in the literature, either using thermal initiation, photochemical conditions, or alternative methods[2,3]. Alkylboronic esters such as boronic esters are highly advantageous and appealing synthetic intermediates for various transformations due to their stability and convenient handling and they can be easily modified[4]. Herein, we present a novel photochemical ATRA protocol where the iodo-reagent ICH_2Bpin, is activated using cheap ascorbic acid and Kessil LED 370 nm (2nd GEN) irradiation which enables its homolytic scission. The protocol was applied for the addition of ICH_2Bpin onto double bonds forming 1,3-iodoboronates which were converted one-pot to cyclopropanes although the unstable boronic intermediates has also been isolated[5]. Furthermore, the photochemical ATRA protocol has also been utilized to a cyclization reaction which led to the synthesis of cyclopetanes via α-boryl radicals which can be further modified. In all cases,the desired products were obtained in good to high yields. The reaction mechanism was extensively examined, revealing the formation of a halogen-bonded complex which initiates the process.

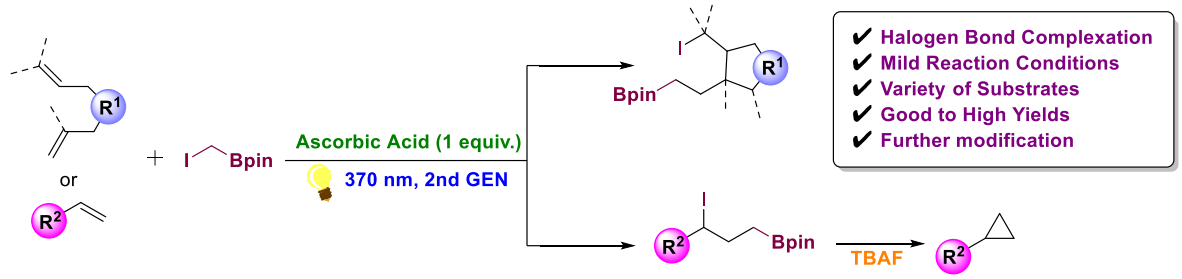

Figure 1. Photochemical ATRA reaction between alkenes and ICH_2Bpin using ascorbic acid

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