

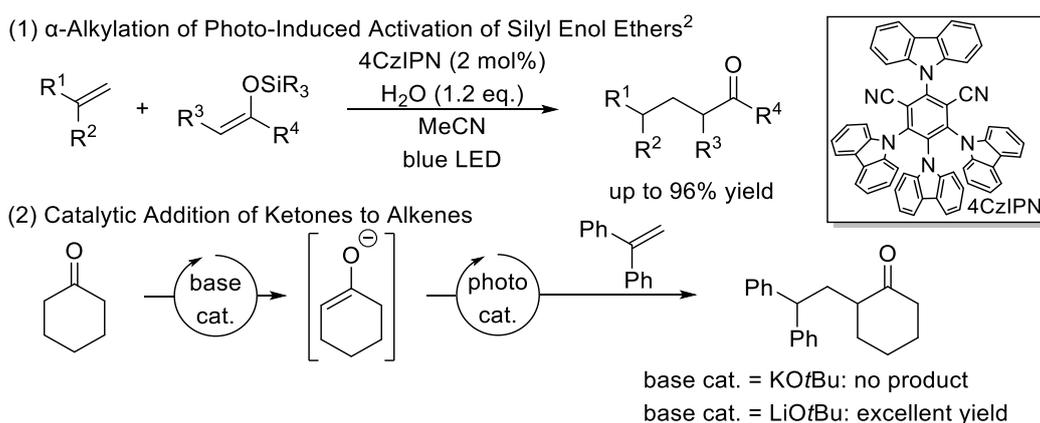
Development of Addition Reactions of Ketones with Alkenes through Photo-Induced Activation of Their Enolates

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α -Alkylation of ketones is one of the most important and fundamental reactions in synthetic organic chemistry. Conventionally, alkyl halides have been employed as alkylating reagents such as Stork enamine alkylation. On the other hand, addition reactions are more efficient than substitution reactions because they proceed without any leaving groups. While enolates of ketones and their equivalents have been utilized to α -functionalization of ketones, their addition reactions with alkenes that afford alkylated ketones are quite slow due to low electrophilicity of alkenes. To overcome this problem, we focused on α -carbonyl radicals that can be prepared through single electron oxidation of enolates.

Initially, silyl enol ethers, which are precursors of α -carbonyl radicals, were employed.¹ In the presence of a photocatalyst, they reacted with alkenes under blue light irradiation to afford the alkylated ketones (eq. 1).² Furthermore, we figured out that approximate 1 equivalent of water to trap silyl cation *in situ* formed was effective to promote the reactions. To the best of our knowledge, this is the first example of intermolecular addition of silyl enol ethers to alkenes. For ideal atom economy, we challenged catalytic formation of enolates (eq. 2). Previously, our group reported Brønsted base-photo hybrid catalyst systems for alkylation of malonates with alkenes.³ Based on this report, KO t Bu was employed as a base catalyst; however, the desired product was not obtained at all. This result was presumably caused by decomposition of the employed photocatalyst under strongly basic conditions. On the other hand, the desired reaction proceeded smoothly in the presence of LiO t Bu. Herein, we report our effort to develop photo-induced addition of ketones to alkenes in detail.



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