

Mechanistic studies of the photosensitized addition of carbon-centered radicals to α,β -enones and butenolides

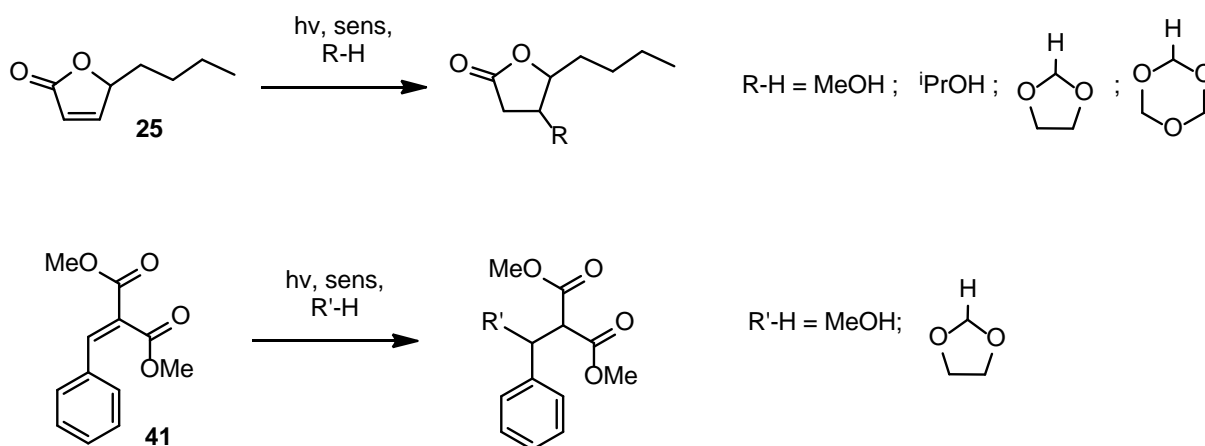
Giacomo Persiani

Master in Chemistry

The formation of a C-C bond has a primary role in organic synthesis. However, traditional methods usually require harsh conditions, involving hazardous materials and having often a poor atom economy. The newly developed methods, although having widely improved synthetic reaction conditions, do not always consider environmental problems. Photochemical reactions occur under unparalleled mild conditions and perfectly fit many criteria of Green Chemistry. Moreover, in many cases they occur in high yields and with high selectivity.

In this sense, an intriguing reaction is the photochemical alkylation of electrophilic alkenes by alkyl radicals. In this process, the reagents are completely incorporated into the products, leading to a 100% atom economy. Furthermore, key radicals are produced in very mild conditions, by catalyzed hydrogen abstraction using a photosensitizer.

In this work, we performed the regio and stereoselective photocatalyzed addition of alcohols and acetals on α,β -enones and butenolides. These reactions occurred in good yields (up to 86%) and in very mild conditions. In particular, we focused our efforts on establishing the mechanism of the photosensitized addition of methanol on butylbutenolide **25**. These mechanistic studies were based on isotope incorporation analyses and determination of the reaction quantum efficiency, which required also the calibration of the light sources by chemical actinometry.



Prof. Christian G. Bochet