

Photochemistry of ethyl esters of α -oxo-carboxylic acids

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The photochemistry of ethyl esters of α -oxo-carboxylic acids of the type $\text{RCOCO}_2\text{CH}_2\text{CH}_3$ was examined using a combination of steady state irradiation and laser flash photolysis techniques. The experimental results indicate that the photoreaction occurs from both singlet and triplet excited states. The product distribution is consistent with a Norrish type II mechanism as the main photodecomposition path; however in the α -ketoester with primary α -hydrogen atoms on the carbonyl group side, an appreciable contribution of type I photofragmentation is observed. Furthermore, the fraction of products arising from the singlet state increases with increasing α substitution. The kinetic data show a greater dependence of the biradical formation rate constant on α substitution at the carbonyl side, than that observed in other α -oxo-esters previously studied. © 1990.