

PHOTOCHEMICAL [3 + 2] CYCLOADDITION OF β -CYANOENONES TO ALKENES

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We have recently found that β -cyanoenones such as 6-cyanouracils or 3-cyano-5,5-dimethyl-2-cyclohexenone undergo unusual photoaddition to alkenes resulting in 1,4-transfer of a cyano group or the formation of [3 + 2] cycloadducts. In further extending this study, we have investigated the photochemistry of 2-cyanochromones to alkenes. Irradiation of 2-cyanochromone (1) and excess isobutene in methanol with Pyrex-filtered light (> 290 nm) under nitrogen atmosphere produced [3 + 2] cycloadduct 2 (81%) together with a minor amount of cyclobutane 3 (12%). The product ratio showed a striking dependency on the reaction temperature; as the reaction temperature was raised, the yield of [3 + 2] cycloadduct increased at the expense of cyclobutane. The photoreaction has also proved to be highly sensitive to oxygen. In the presence of oxygen, the same irradiation of 1 and isobutene in methanol gave rise to an oxygenated adduct 4, while the formation of cyclobutane 3 was not affected. Sensitization and quenching experiments established that both of 2 and 3 were originated from the triplet state of 1.

On the other hand, photoaddition of 2-cyano-3-methylchromone (5) to isobutene in methanol produced the solvent-incorporated adduct 6 (45%) and cyclobutane 7 (40%). The reaction mechanism involving 1,4-biradical intermediate has been proposed.

