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VARIOUS PHOTOREACTIVITIES OF ALPHA SUBSTITUTED ORTHO-METHYLACETOPHENONES

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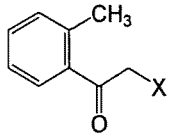
Photochemiatry of ortho-methylacetophenone has been extensively studied for decades. The excited triplet ketone undergoes fast intramolecular hydrogen abstraction to yield a biradicaloid species, the triplet enol. Decay of the species results in the formation of two ground state intermediates, the xylyl enols of Z and E configurations. The Z isomer has a short lifetime and gives the starting compound via an intramolecular [1,5] H-shift. The E isomer, on the other hand, has a relatively long lifetime and can participate in various photoreactions including the formation of benzocyclobutenols. Bergmark showed an interesting twist of photoreactivities of these systems by putting a chlorine at the alpha position to the carbonyl group. Irradiation of the alpha-chloro(o-methyl)acetophenone (1) results in the formation of an indanone via efficient release of the chlorine followed by cyclization.

We have recently reported an interesting contrast in photoreactiviyies of a-chloro- and bromo valerophenones. a-Bromovalerophenone gives only the C-Br bond cleavage products, but a-chlorovalerophenone follows the classical Norrish/Yang reaction pathway predominantly. In order to see if the dramatic changes of the reaction routes can also be applied to the Bergmark system, alpha-bromo(o-methyl)acetophenone (2) was synthesized and irradiated under the same irradiation condition. Photolysis of 2gives (o-methyl)acetophenone mainly and the indanone formation was not observed, which is in good contrast to Bergmark system. We also prepared alpha-benzoyloxy(o-methyl)acetophenone (3) and alpha-pyridinium(o-methyl) acetophenone bromide (4) and their photoreactivities were investigated. In this report the photochemical behaviors of the compounds 1-4will be compared with each other and the mechanistic reasoning of the different reactivities will be discussed.



1: X = Cl
2: X = Br
3: X = OC(=O)Ph
4. X = pyridinium bromide