AZETIDINE-2,4-DIONES VIA PHOTOINDUCED RING CONTRACTION OF SUCCINIMIDES

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Photolysis of an acetonitrile solution of N-methylcyclohexane-1,2-dicarboximide (1) gave a ring contracted product N-methylcyclohexane-1,1-dicarboximide (2) (mp 96-97°C, 17%) together with a small amount of N-formyl-N-methyl-1-cyclohexene-1-carboxamide (3) (3%). The starting material recovered (60%) was partly isomerized to its trans isomer. When treated with methylamine, 2 gave N,N'-dimethylcyclohexane-1,1-dicarboxamide quantitatively, and further photolysis of 2 in methanol gave methyl cyclohexanecarboxylate (35%) and 5-methoxy-4,4-pentamethylene-2-methyl-isoxazolid-3-one (60%). Similarly, irradiation of succinimide derivatives gave the corresponding azetidine-2,4-diones.

A mechanism involving two photon process is proposed. First, 1 undergoes α-cleavage reaction to give a biradical, which produces 3. The product 3 will absorb light once again to give a 1,4-biradical, which could collapse to 2. The following experiments support this mechanism. First, irradiation of an acetonitrile solution of 3 gave 2. Secondly, at 254nm the extinction coefficient of 3 is about ten times larger than that of 1. Thirdly, the time dependent variation of 2 and 3 suggests that 3 should be an intermediate of 2. Further, photolysis of N-formyl-N-methyl-α,β-unsaturated amides like 3 gave the corresponding azetidine-2,4-diones in much better yield.