Photochemical Reaction of the Cyclic Enamide, 1-Methyl-1,2,3,4,5,6,7,8-octahydro-2-quinolone

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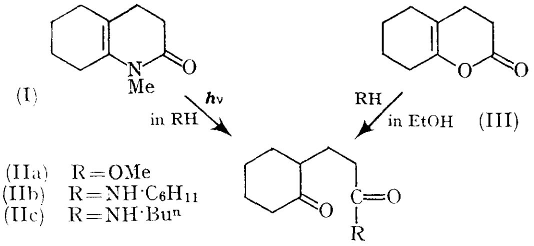
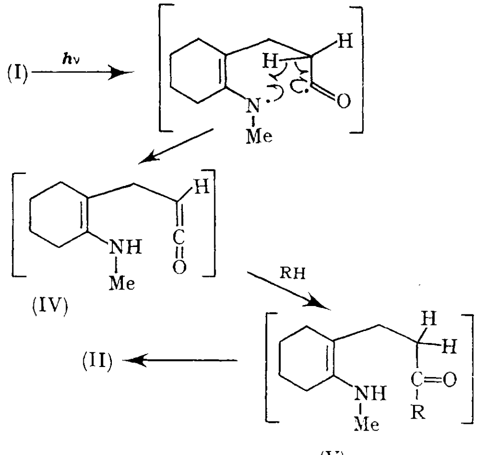
RECENTLY, Yang[1] and Hoffmann[2] reported that the photolysis of enamides in methanol gave vinylogous amides by acyl rearrangement. We investigated the photochemical behaviour of the cyclic enamide, 1-methyl-1,2,3,4,5,6,7,8-octahydro-2-quinolone (I)[3] in methanol, cyclohexylamine, and n-butyl-amine. Compound (I) was found to undergo α-cleavage[4] to give the oxocarboxylic acid derivative.



(IIa) R=OMe
(IIb) R=NH·C_6H_{11}
(IIc) R=NH·Bu^n

A solution of (I) in methanol (2·7 g.l.$^{-1}$), through which dry nitrogen was bubbled, was irradiated for 4 hr. with a 300 w high-pressure mercury lamp enclosed in a quartz well. Chromatography of the products on alumina gave methyl 2-oxocyclohexanepropionate (IIa) (13%), starting material (I) (17%) and some unidentified products. Compound (IIa) was identified by comparison with an authentic



(V)

sample.[5] Irradiation of (I) in cyclohexylamine (3 hr.) and n-butylamine (3·5 hr.) under similar conditions gave *N*-cyclohexyl-2-oxocyclohexanepropionamide (IIb) (34%) and *N*-n-butyl-2-oxocyclohexanepropionamide (IIc) (35%), respectively. Compounds (IIb) and (IIc) were identified by comparison with authentic samples which were synthesized by the reaction of the corresponding amines with 3,4,5,6,7,8-hexahydrocoumarin (III) in ethanol.

The photochemical behaviour of the cyclic enamide is analogous to that of cycloalkanone.[4] The reaction may be formulated through a keten intermediate (IV). The enamine (V) formed will then undergo hydrolysis to give the oxocarboxylic acid derivative (II) as the product.

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