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PHOTOCYCLIZATION OF α,β-UNSATURATED AMIDES VIA HYDROGEN ABSTRACTION BY THE β-CARBON ATOM

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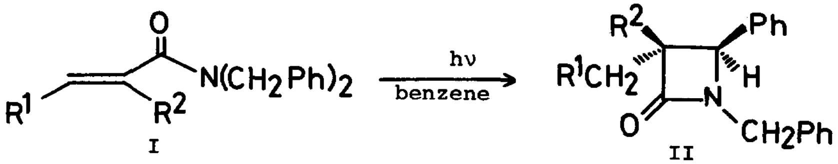
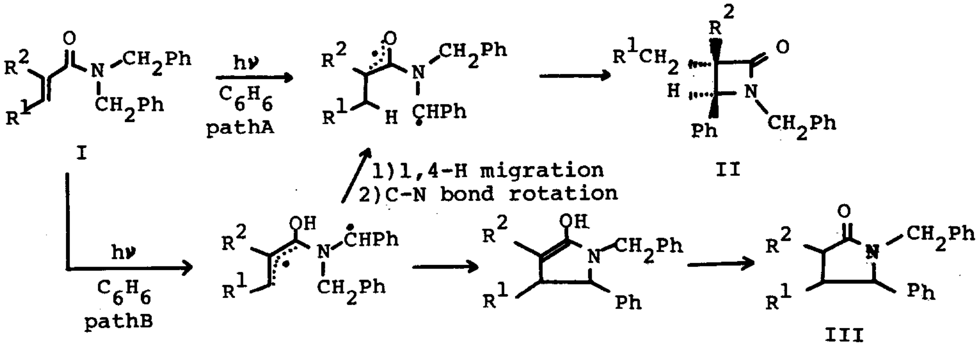
Photochemistry of α,β-unsaturated carbonyl compounds has been studied extensively. Although photocyclization via intramolecular hydrogen abstraction by the β-carbon atom in cyclopentenones¹⁾ and 1-acylcyclopentenes²⁾ has been reported, much less is known about that reaction in acyclic α,β-unsaturated carbonyl compounds. We wish to report photocyclization of α,β-unsaturated amides to 2-azetidinones³⁾ via unprecedented intramolecular hydrogen abstraction by the β-carbon atom in the simple acyclic α,β-unsaturated carbonyl system. Benzene sensitized irradiation of N,N-dibenzyl acrylamide (Ia) with a low pressure mercury lamp under nitrogen gave 1-benzyl-3-methyl-4-phenyl-2-azetidinone (IIa) in 70% yield. The structure of IIa was determined by the direct comparison with an authentic sample.⁴⁾⁵⁾ A trace of the cis isomer was also detected.

Benzene sensitized irradiation of the amides Ib and Ic under the similar conditions also gave the corresponding 2-azetidinones IIb and IIc, respectively. The structures of IIb and IIc were elucidated by use of the spectral data (ir and nmr). The trans conformation of C(3)-ethyl and C(4)-phenyl groups in IIb was estimated by using the nmr spectrum. On the other hand irradiation of N,N-dimethyl acrylamide gave no 2-azetidinones.



	yield(%)
a; $R^1=R^2=H$	70
b; $R^1=Me$, $R^2=H$	30
c; $R^1=H$, $R^2=Me$	84

The formation of IIa-c can be explained in terms of photocyclization via hydrogen abstraction by the β-carbon atom through the six membered transition state as shown below (path A). An alternative path B, which involves hydrogen transfer through the five membered transition state by the amide carbonyl oxygen followed by 1,4-hydroben migration and the rotation of the carbon-nitrogen bond, may be improbable since no 2-pyrrolidinones (III) were formed in all cases.



Irradiation of Ia in benzene with a high pressure mercury lamp also gave IIa slowly, and the formation of IIa was efficiently sensitized by p-methoxyacetophenone. On the other hand direct irradiation of Ia in n-hexane with a low pressure mercury lamp gave IIa in a lower yield with some by-products. These results indicate that the 2-azetidinones were produced from the triplet excited state of the amides

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