PHOTOSENSITIZED OXYGENATION OF 1,3-OXAZEPINES

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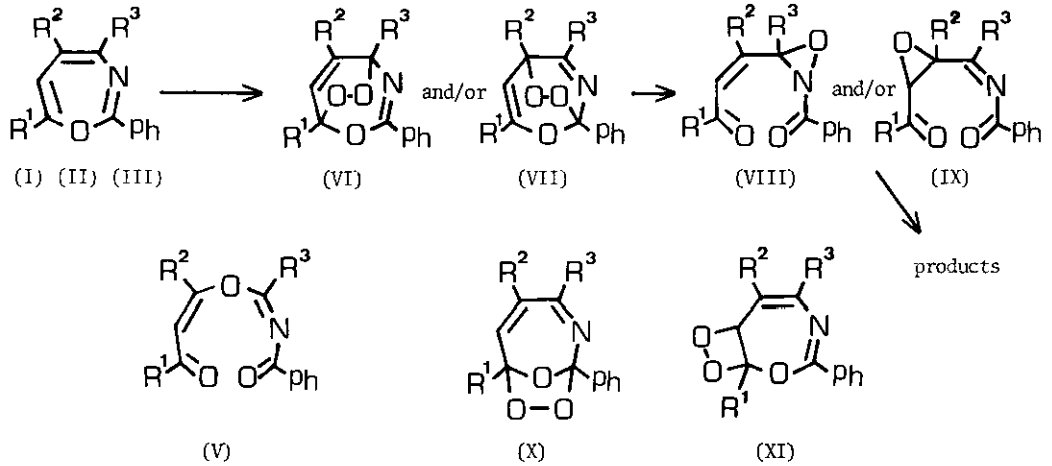
Previously we reported that the dye-sensitized photooxygenation of 2-phenyl-1,3-oxazepine afforded several fragmentation products which were considered to arise from the 1,2-, 1,6- and 1,4-addtion of singlet oxygen. In order to clarify the reaction mechanism, we investigated the photooxygenation of three phenyl-substituted derivatives, 2,7-diphenyl-(I), 2,5,7-triphenyl-(II) and 2,4,5,7-tetraphenyl-1,3-oxazepines (III).

When (I) was photooxidized in CCl_4 by bubbling of oxygen under the irradiation with 55x6 W Na-lamp in the presence of TPP (meso-tetraphenylporphine) as a sensitizer, 1-(N-benzoylamino)-4-phenyl-2-buten-1,4-dione (IV), N-(2-formyl-3-oxo-3-phenyl-1-propenyl)-benzamide and N-formylbenzamide were produced in 20, 13 and 30 % yields, respectively. Compound (IV), which was purely isolated as a precipitate from the reaction mixture, was readily cyclized to afford N-benzoyl-5-hydroxy-5-phenyl-Δ^3-pyrroline-2-one. The similar types of products were also obtained in the photooxidation of triphenyl-1,3-oxazepine (II). On the other hand, photooxidation of tetraphenyl-1,3-oxazepine (III) afforded vinyl ether (V) in 25 % yield, along with N-(2-benzoyl-1-phenyl-vinyl)-dibenzamide and N-(2-benzoyl-3-oxa-1,3-diphenyl-1-propenyl)-benzamide in 17 and 25 % yields, respectively. Vinyl ether (V) was labil to moisture and easily decomposed to benzoylmethane and dibenzoylamine quantitatively.

All these products can be derived from 4,7- and/or 2,5-endo-peroxides (VI) and (VII) via oxaziridine (VIII) and epoxide (IX). Other expected intermediates (X) and (XI) are not suitable for the formation of all oxidized fragment products.



(I) (II) (III) (VI) (VII) (VIII) (IX)

(V) (X) (XI)