

PHOTOSENSITIZED OXYGENATION OF 1,3-OXAZEPINES

Akibiko Tokida, Keiji Okada and Toshio Mukai

Department of Chemistry, Faculty of Science, Tohoku University

Aoba, Aramaki, Sendai 980, Japan

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-addition 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 labile 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.

