

PHOTOCHEMICAL RING-CONTRACTION REACTIONS OF BENZ[d]-
3,1-OXAZEPINES HAVING NO SUBSTITUENT AT THE 5-
POSITION TO INDOLE-3-CARBOXALDEHYDES¹

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Irradiation of 5-unsubstituted benz[d]-3,1-oxazepines having phenyl or cyano group at the 2-position with high-pressure mercury lamp without filter resulted in the formation of 2-phenyl- or 2-cyanoindole-3-carboxaldehydes in good yields. The corresponding quinoline 1-oxides can directly be converted to the indole-3-carboxaldehydes by irradiation (254 nm rays) in acetonitrile without isolating the oxazepines.

It is well known that benz[d]-3,1-oxazepine derivatives are formed by irradiation (≥ 300 nm) of quinoline 1-oxides.² However, very little is known hitherto about the photoreactivity of benz[d]-3,1-oxazepines thus formed.^{3,4} We have found that 5-unsubstituted benz[d]-3,1-oxazepines can be converted to indole-3-carboxaldehydes by irradiation of 254 nm rays.

Irradiation of 2-cyanobenz[d]-3,1-oxazepine^{3,5} (2a), 620 mg, in 1 l of acetonitrile with high-pressure mercury lamp (Toshiba 400P) in a quartz vessel for 3 hrs gave, after chromatography over silica gel, 500 mg of pale yellow crystals (3a) as the sole isolable product, C₁₀H₆ON₂; mp 229-230° (dec., softening at 207°). It gave the hydrazone, C₁₀H₈N₄; mp 270°, and the phenylhydrazone, C₁₆H₁₂N₄; mp 204-205°. The IR spectrum of 3a (KBr) exhibited the characteristic band of cyano group (2220 cm⁻¹) together with bands at 1650 (CHO) and at 3150 cm⁻¹. All of these data indicate that 3a is 2-cyanoindole-3-carboxaldehyde.

In a similar way, one can obtain two other indole-3-carboxaldehydes (3b⁶; mp 250-252°, and 3c; mp 201-202°) from the corresponding oxazepines (2b³, and 2c⁷) again in satisfactory yields (ca. 55%). Just like as indole-3-carboxaldehyde,⁸ the UV maxima of these products shift in alkaline solution (Table I). In these photolyses, methanol can also be used as a solvent.

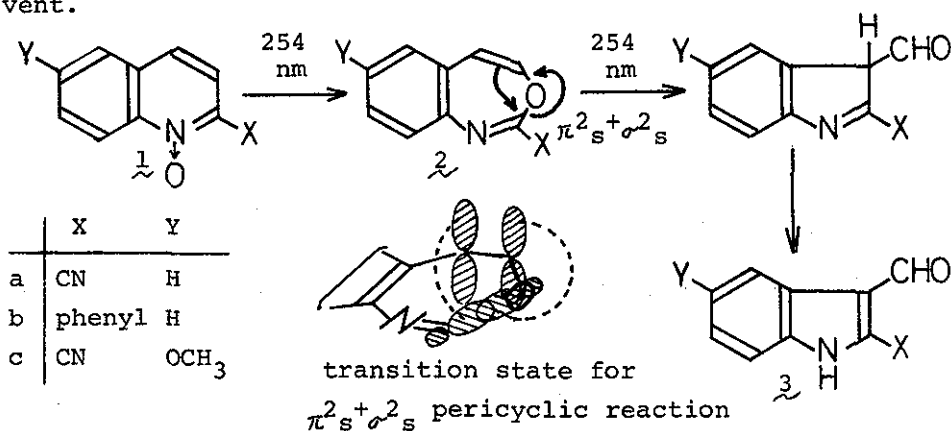


Table I. UV Spectra of Indole-3-carboxaldehydes (3a-3c).

Comp.	Solvent	λ_{\max} : nm (log ϵ)	
	CH ₃ OH		aq. 5%-KOH
<u>3a</u>	216 (4.54), 243.5 (4.32), 250 (sh. 4.26), 314 (4.15)	222 (4.46), 268 (4.37), 320 (sh. 3.98), 352 (4.16)	
<u>3b</u>	220.5 (4.36), 257.5 (4.51), 314 (4.20)	233 (4.29), 274 (4.47), 337 (4.25)	
<u>3c</u>	219.5 (4.39), 246 (4.26), 253.5 (4.24), 275.5 (3.82), 315.5 (4.08), 350 (sh. 3.90)	220 (4.33), 272 (4.34), 345 (4.18)	

The most reasonable explanation of this novel ring-contraction reaction would be a $\pi_s^2 + \sigma_s^2$ process as depicted in the Scheme.⁹ The similar mechanism has been proposed to account for the photochemical formations of 2-cyanoskatole from 5-methylbenz[d]-3,1-oxazepine³ and of 3-vinylindazole from 3H-1,2-benzodiazepine.¹⁰ Very recently, Tsuchiya *et al.* has gained a strong supporting evidence for the above mechanism by photolysis of 3-acetoxy-3H-1,2-benzodiazepine affording stereospecifically an indazole having trans-oriented ethylene function at the 3-position.¹¹

It is also confirmed that these oxazepines were not necessarily isolated. Hence, the corresponding quinoline 1-oxides (1a-1c) were irradiated by high-pressure mercury lamp with Pyrex filter until all of the N-oxides were consumed, then the filter was taken off and the irradiation was again continued until the oxazepines (2a-2c) were consumed. To this

purpose, it is more convenient to irradiate the N-oxide without the filter at the beginning. Under these conditions, the indole-3-carboxaldehydes (3a-3c) can be obtained in ca. 40-50% yields (based on the N-oxide used).

Such a technique seems to make possible to prepare indole-3-carboxaldehydes from the oxazepines which are too unstable to be isolated (it is well known that most of the oxazepines having hydrogen or alkyl group at the 2-position are very easily solvolyzed and thus can not be isolated as such.²). In the preliminary examination, we have identified indole-3-carboxaldehyde (a few % yield) in the irradiated solution of quinoline 1-oxide in dry acetonitrile by the same light source without filter.¹²

It should be noted that since the photo-conversion of quinoline 1-oxides having hydrogen or alkyl group at the 2-position to benz[d]-3,1-oxazepines is prevented to occur in a hydroxylic solvent,^{2,13} the use of methanol instead of acetonitrile in the photolysis of quinoline 1-oxide itself resulted in an almost exclusive formation of carbostyryl.^{14,15}

Acknowledgement Thanks are due to Messrs. T. Kimata and T. Maekawa, and Miss. Y. Hamashita for the co-operation in a part of this work.

References and Notes

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Received, 15th November, 1976