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

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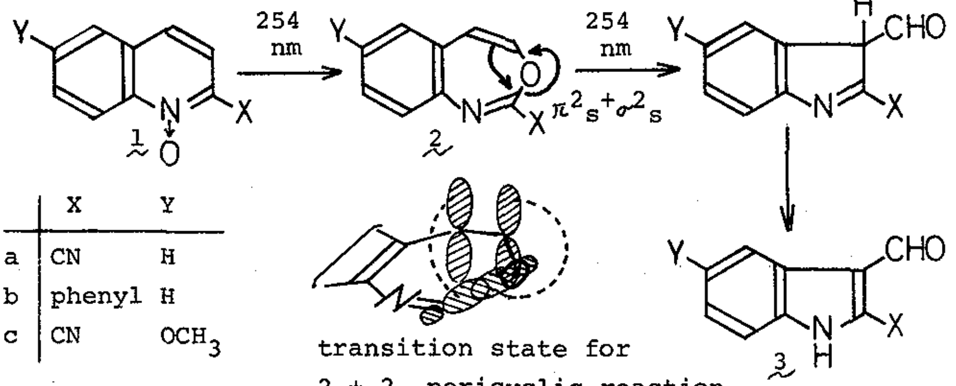
Irradiation of 5-unsubstituted benz[d]-3,1-oxazepines having phenyl or cyano group at the 2-position with high-pressure mercury lamp without filter resulted in the formation of 2-phenyl- or 2-cyanoindole-3-carboxaldehydes in good yields. The corresponding quinoline 1-oxides can directly be converted 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 ($\gtrsim$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 quarz vessel for 3 hrs gave, after chromatography over silica gel, 500 mg of pale yellow crystals (3a) as the sole isolable product, $C_{10}H_6ON_2$; mp 229-230° (dec., softing at 207°). It gave the hydrazone, $C_{10}H_8N_4$; mp 270°, and the phenylhydrazone, $C_{16}H_{12}N_4$; 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 (3b[6]; mp 250-252°, and 3c; mp 201-202°) from the corresponding oxazepines (2b[3], and 2c[7]) 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.



	X	Y
a	CN	H
b	phenyl	H
c	CN	OCH_3

transition state for $\pi^2{}_s+\sigma^2{}_s$ pericyclic reaction

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

Solvent / Comp.	CH_3OH	aq. 5%-KOH
	λ_{max}: nm (log ε)	
3a	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)
3b	220.5 (4.36), 257.5 (4.51), 314 (4.20)	233 (4.29), 274 (4.47), 337 (4.25)
3c	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 ${}_{\pi}2_{s} + {}_{\sigma}2_{s}$ 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-oxazepine[3] 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 carbostyril.[14,15]

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