Tetrahedron Letters No.43, pp. 4519–4521, 1968. Pergamon Press. Printed in Great Britain.

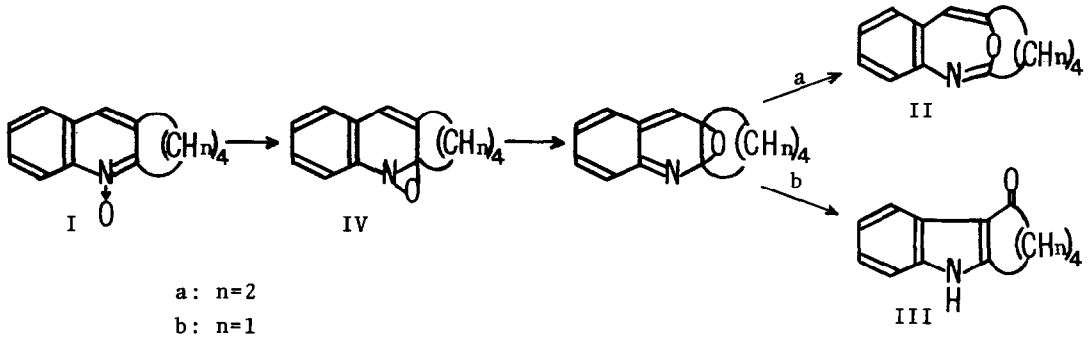
THE PHOTOLYSIS OF ACRIDINE N-OXIDE TO CYCLOHEPT[b]INDOL-10(5)-ONE[1)]

Masayuki Ishikawa, Chikara Kaneko, and Sachiko Yamada

Institute for Medical and Dental Engineering, Tokyo Medical and Dental University, Bunkyo-ku, Tokyo, Japan

(Received in Japam 28 June 1968; received in UK for publication 27 July 1968)

In an earlier communication[2)] we reported that the irradiation (>300 mμ) of tetrahydroacridine N-oxide (Ia) in an aprotic solvent (benzene or dichloromethane) resulted in the formation of two isomeric products, 2,7-tetramethylene-benz[d]-1,3-oxazepine (IIa) and 5,6,7,8,9,10-hexahydrocyclohept[b]indol-10(5H)-one (IIIa) in the respective yield of 70 and 10%, together with 8% of tetrahydroacridine, and postulated evidence for the existence of two different pathways (a and b) from the common oxaziridine intermediate[3)] (IVa) in the formation of IIa and IIIa.



a: n=2
b: n=1

In an attempt to obtain 3,4-benz-1,6-oxido[10]-2-azaannulene (IIb), acridine N-oxide[4)] (Ib) was irradiated in benzene or dichloromethane. Contrary to our expectation, IIb was not obtained but cyclohept[b]indol-10(5H)-one (IIIb) was formed in 70-80% yield, together with a small amount (ca. 2.5%) of acridine.

In a typical run, 500 ml. of CH_2Cl_2 solution containing 500 mg. of Ib was irradiated for 3.5 hrs. by 100 W high-pressure mercury lamp (Hanovia) with a Pyrex filter. Concentration of the solvent to ca. 10 ml. followed by filtration

and recrystallization of the product from methanol afforded 350 mg. of pale green plates, m.p. 285-286°; Anal. found for $C_{13}H_9ON$: C, 79.88; H, 4.69; N, 7.27. The UV, IR, and NMR spectra of the photo-product are shown in Table I. The mother liquor afforded by silica gel chromatography, 13 mg. of acridine and 40 mg. of the above photo-product.

TABLE I.

Spectroscopical Data of the Photo-product (IIIb)

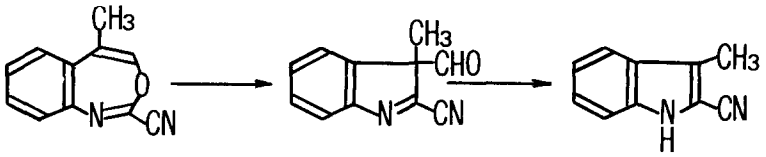
	UV	IR	NMR (DMSO-d_6)
Solvent	λ_{max} mμ (log ε)	ν_{max}^{KBr} cm^{-1} (intensity)[b]	Chemical Shift (τ) [J in Hz]
95% EtOH	218 (4.55) 237 (4.42)	3060-2700 (broad m)	−2.53 (singlet, 1H)
	281 (4.37) 362[a] (3.92)	1635 w	1.18 (doublet, 1H) [8.0]
	376 (4.01) 396 (3.91)	1550 m	2.2-3.0 (multiplet, 7H)
5% KOH	242[a] (4.32) 275 (4.23)	1516 s	
	315 (4.68) 402 (3.74)	1480 s	
		807 m	
1N HCl	231 (4.42) 254 (4.21)	755 s	
	271 (4.21) 308 (4.55)	716 m	
	375[a] (3.64)		

a shoulder peak

b w=weak; m=medium; s=strong

The UV spectrum of the photo-product was not identical with any acridinol,[5] and its NMR spectrum eliminated the oxido-azaannulene structure (IIb) for this compound. By catalytic reduction with 5% palladium charcoal in methanol, the photo-product absorbed two moles of hydrogen and was transformed in a quantitative yield to the tetrahydro compound as colorless prisms, m.p. 220-221° (recrystallized from methanol); Anal. found for $C_{13}H_{13}ON$: C, 78.29; H, 6.62; N, 7.0. The tetrahydro compound was identified with IIIa[2] by mixed melting point determination and from the comparison of their IR (ν_{max}^{KBr} cm^{-1}: 3170, 1603, 1580, 1440, and 753) and UV ($\lambda_{max}^{95\%\ EtOH}$ mμ (log ε): 213.5 (4.48), 245 (4.19), 268 (4.07) and 302 (4.09)) spectra. This fact and the spectroscopical data of the photo-product shown in Table I clearly demonstrate that the photo-product is cyclohept-[b]indol-10(5H)-one (IIIb).

The failure in the isolation of IIb is due either to a high rate ratio of step b to step a[6] or to the facile photo-isomerization of IIb to IIIb under these conditions. The latter possibility is supported by the observation that 6-methylbenz[d]-1,3-oxazepine-2-carbonitrile (V) undergoes photo-isomerization (very fast by 253.7 mμ ray but slow by >300 mμ ray) to 3-methyl-2-cyanoindole (VI) in a quantitative yield, either in protic or in aprotic solvent.[7,8]



V VI

The periodical UV measurements of 10^{-5} molar solution of Ib in CH_2Cl_2 irradiated by >300 mμ ray could not detect the formation of any transient formation of the unstable intermediate and, therefore, if IIb is formed, its photo-isomerization to IIIb should be very fast.

Acknowledgements A part of the expense of this work was defrayed by a grant (to C. K.) from the Fuji Photo Film Co., Ltd., which is gratefully acknowledged.

References

1) Part III of the series entitled "Photochemistry of Heterocyclic Compounds." by M. Ishikawa and C. Kaneko. Part II: M. Ishikawa, C. Kaneko, I. Yokoe, and Sa. Yamada, Tetrahedron, in press.
2) C. Kaneko, Sa. Yamada, I. Yokoe, and M. Ishikawa, Tetrahedron Letters, 1967, 1873.
3) The intermediary formation of the oxaziridine species in the photolysis of some quinoline 1-oxides has been suggested strongly by the trapping experiment: C. Kaneko, I. Yokoe, and M. Ishikawa, Tetrahedron Letters, 1967, 5237.
4) Irradiation of Ib in ethanol gave rise to N-hydroxy-9-ethoxyacridane as the main product: H. Mantsch and V. Zanker, Tetrahedron Letters, 1966, 4211.
5) A. Albert and L.N. Short, J. Chem. Soc., 1945, 760.
6) Irradiation of 2,3-trimethylenequinoline 1-oxide under these conditions gave exclusively 4-oxo-1,2,3,4-tetrahydrocarbazole and this fact has been explained from the instability of the corresponding oxazepine.[2]
7) C. Kaneko and Sa. Yamada, Chem. Pharm. Bull. (Tokyo), 14, 555 (1966).
8) C. Kaneko, J. Syn. Org. Chem. Japan, in press.