Since the photolysis in alcoholic solvents invariably resulted in the formation of the corresponding indole derivatives (X—XII) as the minor isomerization products, it can be concluded that two pathways (1,3-oxygen rearrangement and carbonium ion rearrangement processes) are operating simultaneously under these conditions, though the products *via* the carbonium ion rearrangement process (path *b*) predominate. The mechanism shown as path *b* in Chart 2 can be reasonably postulated to account for the formation of these spiro compounds.

As a comparative experiment, photolysis of 2,3-trimethylenequinoline 1-oxide (XIII) in methanol or in ethanol was carried out and, in agreement with a high energy requirement of cyclobutane structure in a typical carbonium ion rearrangement reactions, such as dienone-phenol rearrangement,¹⁷⁾ no spiro compound (XXIV) was detected in the reaction mixture, and 4-oxotetrahydrocarbazole (XIV) and the parent base were obtained in the respective yields of 60 and 7% as in the photolysis in benzene solution. The data presented herein, therefore, proved the correctness of our previous postulation summarized in Chart 1.

Acknowledgement The authors thank the Fuji Photo Film Co., Ltd., for maintenance grant (to C.K.). The authors are indebted to Prof. S. Sakai of the Chiba University for the determination of mass spectra and to Dr. Y. Kawazoe of the National Cancer Center Research Institute (Tokyo) for the determination of NMR spectra.

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Received March 14, 1969

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[Chem. Pharm. Bull.]
17(6)1294—1297(1969)

UDC 547.835.1.04 : 541.144

Photochemistry of Heterocyclic Compounds. (5).¹⁾ The Photolysis of 9-Cyanoacridine 10-Oxides: The Synthesis of Benzo[*c*]-2-aza-1,6-oxido[10]annulenes, Oxepino[2,3-*b*]quinolines, and 11-Cyano-6-oxo-6H-azepino[*a*]indoles

As part of our continuing study on the photochemical behavior of aromatic amine N-oxides,²⁾ we have examined the light-induced reactions of 9-cyanoacridine 10-oxides (Ia and Ib).

Photolysis of Ia, b with a high-pressure mercury vapor lamp (450W, Hanovia, Pyrex filter) produced four products, all having identical elemental composition with the starting N-oxides, the 2-aza-1,6-oxido[10]annulenes (IIa, b), the azepinoindoles (IIIa, b), the oxepino[2,3-*b*]quinolines (IVa, b), and the oxabicyclo[3.2.0]heptadiene derivatives (Va, b), together with a small amount (2—5%) of the parent amines (VIa, b).

- 1) Part (4): C. Kaneko, I. Yokoe, Sa. Yamada, and M. Ishikawa, *Chem. Pharm. Bull.* (Tokyo), **17**, 1290 (1969). This paper also forms Part XV of "Studies on the N-Oxides of π -Deficient N-Heteroaromatics."
2) C. Kaneko, *J. Synthe. Org. Chem. Japan (Yūki Gōsei Kyōkaishi)*, **26**, 758 (1968), and the references cited therein.

TABLE I. Irradiation Products of Ia and Ib^{a)}

Product No.	R	Yield (%) ^{b)}		mp (°C)	m μ	UV $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$	log ϵ
		Irradiation solvent					
		Benzene	Methanol				
IIa	CH ₃	3—5	ca. 1	173—174.5	282.5, 385	4.63, 3.91	
IIIa	CH ₃	5—6	ca. 2	210—212	(263, 293, 316, 415)	(4.16, 4.37, 4.36, 3.76)	
IVa	CH ₃	8—10	9—10	161—162	(236, 264, 354, 385)	(4.56, 4.34, 4.06, 4.12)	
Va	CH ₃	11—12	18—20	179—180	(264, 306, 356, 371, 318)	(4.34, 3.82, 4.01, 4.05, 3.83)	
IIb	H	2—3	—	132—135	276, 375	4.64, 3.89	
IIIb	H	10—12	—	201—204	(256, 284.5, 312, 415)	(4.04, 4.18, 4.11, 3.59)	
IVb	H	18—22	—	137—138	(345, 258, 367)	(4.32, 3.97, 3.95)	
Vb	H	trace	—	176—177	(260, 304, 315, 345, 359)	(4.24, 3.68, 3.71, 3.88, 3.89)	

a) Irradiation was continued until almost all of the starting N-oxide was consumed.

b) Yields based on unrecovered N-oxide.

Chart 1

TABLE II. NMR Spectra of II to V in $\text{CDCl}_3^{a,b)}$

Compound	H_1, H_2	H_4, H_5	H_7, H_8	CH_3
IIa	2.71 d, 2.95 d ($J_{1,2}=11$)	2.43 s, 1.95 s	2.39 d, 2.08 d ($J_{7,8}=9.5$)	7.42 s, 7.53 s
IIIa	3.40 d, 3.15 d ($J_{1,2}=9$)	2.65 s, 2.41 s	2.65 d, 1.25 d ($J_{7,8}=9$)	7.45 s, 7.65 s
IVa	3.51 d, 4.41 d ($J_{1,2}=6$)	3.15 s, 2.13 s	2.43 d, 2.15 d ($J_{7,8}=9$)	7.95 s, 7.48 s
Va	4.40 d, 3.99 s ($J_{1,2}\approx 0, J_{1,4}=2.5, J_{2,4}=1.0$)	5.38 dd, 2.23 s	2.46 d, 2.19 d ($J_{7,8}=9$)	8.00 s, 7.43 s
Compound	H_1-H_4		H_5-H_8	
IVb	$\text{H}_1=3.51$ d $\text{H}_2=4.33$ t $\text{H}_3=3.67$ t $\text{H}_4=3.00$ d	($J_{3,4}=12, J_{2,3}=J_{1,2}=6$)		1.85—2.55 m
Vb	$\text{H}_1=4.28$ t $\text{H}_2=3.69$ d $\text{H}_3=3.30$ t $\text{H}_4=5.26$ d	($J_{2,3}=J_{1,4}=J_{1,3}=3$)		1.90—2.60 m
$\text{H}_1=3.79$ d $\text{H}_2=4.60$ t $\text{H}_3=4.03$ t $\text{H}_4=3.37$ d	($J_{3,4}=11, J_{1,2}=J_{2,3}=5.5$)
$\text{H}_1=5.20$ t $\text{H}_2=4.16$ dd, $\text{H}_3=3.88$ t $\text{H}_4=6.72$ m	($J_{2,3}=J_{1,4}=J_{1,3}=2.8, J_{2,4}=1.5$)		

a) Chemical shift in τ -units and coupling constant in cps; s, singlet, d, doublet, dd, double doublet, m, multiplet etc.

b) Fine broadening and splitting (with $J \leq 1$) of each signal are not noted.

The structures of II to V were assigned to these photo-isomerization products on the basis of their NMR spectra (Table II). The supporting evidences for II and confirmation of the structures (III—V) were provided further from the reactions to be described below.

Catalytic hydrogenation⁵⁾ of IIa led to 9-cyano-2,7-dimethylacridine⁶⁾ (VIa, ca. 20%) together with at least three products, so far not identified. Reaction of IIa with trace of hydrochloric acid in ethanol at room temperature gave IIIa in 70% yield. IR spectrum (KBr) of IIIa,b showed a carbonyl band at ca. 1670 cm^{-1} region, respectively. Catalytic hydrogenation⁵⁾ of IIIa afforded the tetrahydro compound (VII, ca. 80%), mp $87-91^\circ$, whose IR

3) A. Shani and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 6310 (1967).

4) L.A. Paquette, J.H. Barrett, R.P. Spitz, and R. Pitcher, *J. Am. Chem. Soc.*, **87**, 3417 (1965).

5) Catalytic hydrogenation reaction was carried out in ethanol over palladium-charcoal and the reaction was terminated when slight excess of one (reduction of IIa) or two molar equivalents (reduction of IIIa and IVb) of hydrogen was taken up.

[KBr; 2220, 1720 cm^{-1}] and UV spectra [$\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ $m\mu$ ($\log \epsilon$): 259 (4.16), 284 (4.05), 299 (4.04), 306 (4.02)] indicated the presence of an N-acylindole chromophore.

Catalytic hydrogenation⁵⁾ of IVb led to two products, VIII (50%), mp 110–113.5°, UV [$\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ $m\mu$ ($\log \epsilon$): 250 (4.51), 314 (3.81), 326 (3.88), 338 (3.92)] and IX (20%), mp 185–187°. UV [$\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ $m\mu$ ($\log \epsilon$): 233 (4.36), 294 (3.87), 342 (sh. 3.84), 357 (3.87)] and IR spectra [KBr; 1655 cm^{-1}] of IX indicated clearly that the compound is a 4-cyanocarbostyryl derivative. The formation of IX in this experiment excluded definitely the alternative oxepine structure (X) for IV. Since IVa, b gave in nearly quantitative yields Va, b by irradiation in an appropriate solvent (benzene or methanol), the structures of Va, b were also confirmed.

The mechanistic pathway shown in Chart 1 are tentatively suggested to account for the present reactions.

The oxaziridine⁷⁾ (XI) initially formed presumably leads first to a tetraene oxide (XII) which by valence tautomerization gives rise to the annulene (II), whereas the path indicated in formula XII gives rise to the indole (III). The other tetraene oxide (XIII) might be considered as a direct precursor of the oxepine (IV), which is derived either from the direct rearrangement of XI or *via* XII. It could be shown that the three products (II–IV) are formed by independent routes, since each was recovered unchanged⁸⁾ under the conditions used for its formation.

Irradiation of Ia in methanol also gave the same products (Table I) but the ratio of the products was different from that obtained by photolysis in benzene.

Since the photolysis of acridine 10-oxide in benzene gave cyclohept[b]indol-10(5H)-one (XIVb) as a major product⁹⁾ probably by pathway *d*, presence of a substituent at 9-position of acridine 10-oxide should be significant in these reactions. Similar substituent effect has been found to exist in the photolysis of tetrahydroacridine 10-oxide derivatives.¹⁾

Further attempt to elucidate the detailed mechanism operating in the photolysis of these N-oxides is currently in progress. Such experiments are primarily directed toward the synthesis of azaannulenes related to II, using N-oxides of phenazine, 9-alkyl- and 9-aryl-acridines, and their higher benzenoid compounds, *i.e.*, benzophenazine and dibenzoacridine derivatives.

Acknowledgement The authors thank Prof. Emeritus E. Ochiai for his interest and encouragement, Prof. S. Sakai of the Chiba University for the determination of mass spectra, and Dr. Y. Kawazoe of the National Cancer Center Research Institute (Tokyo) for the determination of NMR spectra. The authors also wish to acknowledge the financial support (to C.K.) of Fuji Photo Film. Co., Ltd., for this work.

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Received March 14, 1969

6) Catalytic hydrogenation of 1,6-oxido[10]annulene, a carbocyclic analog of II, under the same condition led to naphthalene in a high yield.³⁾

7) Most of the photoisomerization of aromatic amine N-oxides has now been rationalized to proceed *via* the corresponding oxaziridine as the unstable intermediates. *cf.* C. Kaneko, I. Yokoe, and M. Ishikawa, *Tetrahedron Letters*, **1967**, 5237, and the references cited therein.

8) The repeated silica gel chromatography of II–IV and irradiation of II and III under identical conditions of their formation assured the stability of these compounds. Since the irradiation of IV caused its irreversible transformation to V, longer irradiation of I resulted in higher product ratio of V/IV.

9) M. Ishikawa, C. Kaneko, and Sa. Yamada, *Tetrahedron Letters*, **1968**, 4519.