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.

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17) N.L. Windler, "Molecular Rearrangements," ed. P. De Mayo, Interscience Pub., N.Y., Vol. 2, 1964, p. 1028.

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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)] Irradiation solvent Benzene	Methanol	mp (°C)	UV $\lambda_{max}^{CH_2Cl_2}$ mμ	log ε
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, 318, 356, 371	(4.34, 3.82, 3.83, 4.01, 4.05
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	(3.97, 4.32, 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.

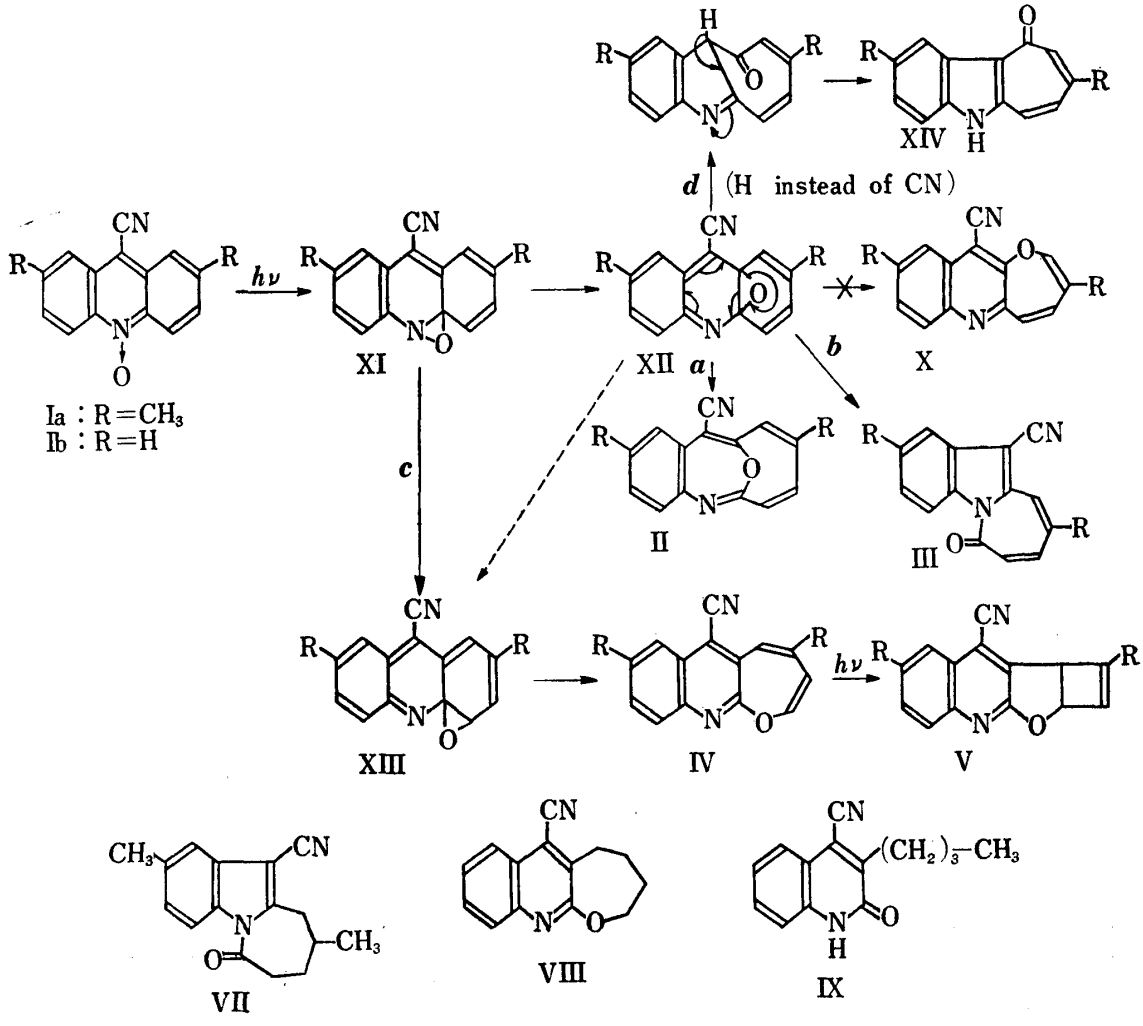
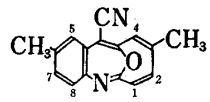
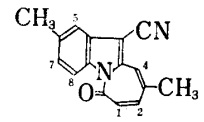
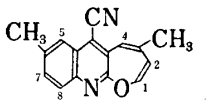
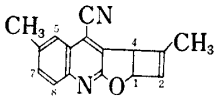
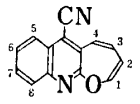
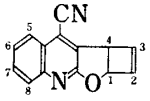
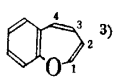
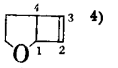


Chart 1

Table II. NMR Spectra of II to V in $CDCl_3$[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 ($J_{1,2}\simeq 0$, $J_{1,4}$=2.5, $J_{2,4}$=1.0)	5.38dd, 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		H_1=3.51 d H_2=4.33 t H_3=3.67 t H_4=3.00 d	($J_{3,4}$=12, $J_{2,3}=J_{1,2}$=6)	1.85—2.55 m
Vb		H_1=4.28 t H_2=3.69 d H_3=3.30 t H_4=5.26 d	($J_{2,3}=J_{1,4}=J_{1,3}$=3)	1.90—2.60 m
	 3)	H_1=3.79 d H_2=4.60 t H_3=4.03 t H_4=3.37 d	($J_{3,4}$=11, $J_{1,2}=J_{2,3}$=5.5)	
	 4)	H_1=5.20 t H_2=4.16 dd, H_3=3.88 t 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 $J\lesssim 1$) 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 hydrogenation[5] of IIa led to 9-cyano-2,7-dimethylacridine[6] (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, respectivly. Catalytic hydrogenation[5] of IIIa afforded the tetrahydro compound (VII, *ca.* 80%), mp 87—91°, 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 [$\lambda_{max}^{CH_2Cl_2}$ mμ (log ε): 259 (4.16), 284 (4.05,) 299 (4.04), 306 (4.02)] indicated the presence of an N-acylindole chromophore.

Catalytic hydrogenation[5] of IVb led to two products, VIII (50%), mp 110—113.5°, UV[$\lambda_{max}^{CH_2Cl_2}$ mμ (log ε):2 50 (4.51), 314 (3.81), 326 (3.88), 338 (3.92)]and IX (20%), mp 185—187°. UV [$\lambda_{max}^{CH_2Cl_2}$ mμ (log ε): 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-cyanocarbostyril 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 oxaziridine[7] (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 unchanged[8] 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 product[9] 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.

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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.