[Chem. Pharm. Bull. 23(11)2818—2834(1975)]

UDC 547.835.1'546.21.04 : 541.14

Studies on the N-Oxides of π-Deficient N-Heteroaromatics. XXIV.*,[1] Photochemistry of Acridine 10-Oxides (1)[2]

Sachiko Yamada,[3] Masayuki Ishikawa,[3] and Chikara Kaneko[3a]

Research Institute for Medical Engineering, Tokyo Medical and Dental University[3]

(Received April 30, 1975)

Photolysis of a series of acridine 10-oxides (Ia—Ig) in various solvents is reported. The structures of photo-products were determined by syntheses, chemical transformation to the known compounds, or by direct examination of their spectroscopic data. Based on the structures of photo-products and the solvent effect on the product distribution in these photolyses, a mechanistic rationalization of these photo-reactions is presented. The characteristic features of the photo-rearrangement reactions of acridine 10-oxides are discussed and compared with those of bicyclic and monocyclic azine N-oxides, *e,g.*, quinoline 1-oxides and pyridine 1-oxides.

Recent experiments have established that photolysis of mono- and bi-cyclic aromatic amine oxides proceeds through an oxaziridine species as a primary photo-product.[4,5] Three pathways (a, b, and c) from this intermediate then account for the formation of photo-rearrangement products.[6] In path a, this intermediate rearranges to the 2-oxo-azine (such as carbostyrils) with concomitant 1,2-shifts of the substituent attached to the carbon atom in the oxaziridine ring.[7] If the substituent of a starting N-oxide is so chosen that no 1,2-shift of the substituent is possible,[1,4,8] the photo-products were the ring enlargement products which arose from the oxygen rearrangement of the oxaziridine (pathway b) or the ring contraction products derived from the 1,2-oxazepine, a valence bond tautomer of the oxaziridine (pathway c).

Thus, the photolysis of 2-cyanoquinoline 1-oxides caused their isomerization to 3,1-benzoxazepine-2-carbonitriles whose formation can be explained by the 1,5-oxygen migration

* Dedicated to the Memory of Prof. Eiji Ochiai.

1) Part XXIII: C. Kaneko, S. Hayashi, and Y. Kobayashi, *Chem. Pharm. Bull.* (Tokyo), **22**, 2147 (1974).

2) Preliminary accounts of a part of this work appeared in the following: *a*) M. Ishikawa, C. Kaneko, and S. Yamada, *Tetrahedron Letters*, **1968**, 4519; *b*) C. Kaneko, S. Yamada, and M. Ishikawa, *Chem. Pharm. Bull.* (Tokyo), **17**, 1294 (1969); *c*) S. Yamada, M. Ishikawa, and C. Kaneko, *Tetrahedron Letters*, **1972**, 977.

3) Location: *Surugadai 2-3-10, Kanda, Chiyoda-ku, Tokyo, 101, Japan*: *a*) To whom inquiries should be addressed.

4) For recent reviews on this topic, see the following: *a*) C. Kaneko, Yukigosei Kyokaishi (*J. Syn. Org. Chem. Japan*), **26**, 758 (1968); *b*) M. Ishikawa and C. Kaneko, *Kagaku no Ryoiki*, **Suppl. 92**, 149 (1970); *c*) G.G. Spence, E.C. Taylor, and O. Buchardt, *Chem. Rev.*, **1970**, 231; *d*) C. Kaneko, *Kagaku no Ryoiki*, **Suppl. 93**, 235 (1970).

5) The formation of oxaziridine species from the photo-excited N-oxides was also supported from the molecular orbital method: *a*) C. Kaneko, S. Yamada, I. Yokoe, and T. Kubota, *Tetrahedron Letters*, **1970**, 2333; *b*) C. Kaneko, *Kagaku Sosetsu*, **1**, 131 (1973), and the references cited therein.

6) This argument can be applied only for the photolysis performed in a neutral solvent system. In an acidified alcohol, for example, an entirely different pathways from this intermediate has been found in the photolysis of some quinoline 1-oxides, C. Kaneko and S. Tanaka, to be published. See also, C. Kaneko, H. Hasegawa, S. Tanaka, K. Sunayashiki, and S. Yamada, *Chem. Lett.*, **1974**, 133.

7) This process in now understood as a typical carbonium ion rearrangement process (a thermal process). See for example, M. Ishikawa, C. Kaneko, I. Yokoe, and S. Yamada, *Tetrahedron*, **25**, 295 (1969).

8) I. Yokoe, M. Ishikawa, and C. Kaneko, *Rep. Res. Inst. Med. Engi., Tokyo Medico-Dental Univ.*, **6**, 18 (1972).

of the oxaziridine followed by a ring-opening.[9,10] In contrast, the photolysis of 2,6-dicyanopyridine 1-oxides resulted in not only the formation of the corresponding 1,3-oxazepines *via* path b, but also of the ring contraction products obviously arisen from the 1,2-oxazepine (path c).[7,11]

These three pathways accounting for the formation of photo-rearrangement products are depicted schematically in Charts 1 ans 2 for pyridine and quinoline 1-oxides, as the respective representatives of those for mono- and bi-cyclic azine N-oxides.[12] Throughout this paper, we depict the stereochemical course of a pericyclic reaction[13] with the arrow symbols proposed recently by one (C.K.) of the present authors.[14] In this symbol representation,

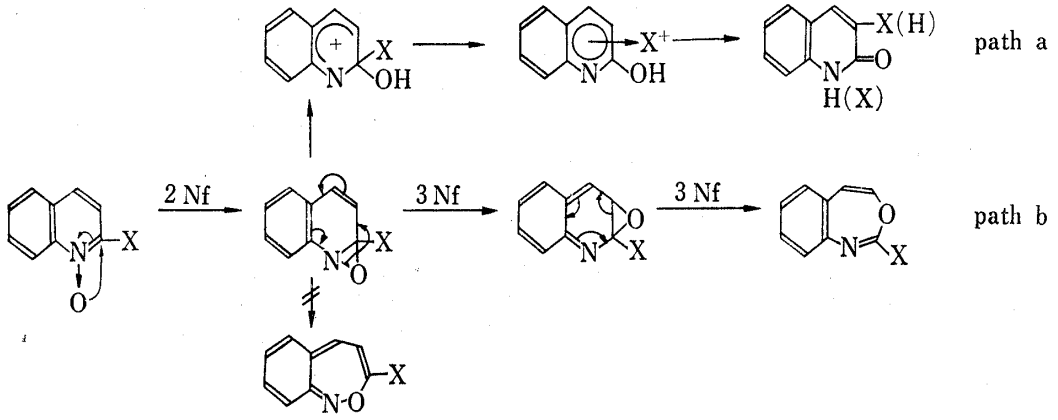


Chart 1. Photo-rearrangement Processes of Quinoline 1-Oxides

a full arrow (——→or⟶) designates a suprafacial use of a bond (π- or σ-bond) in question, while a half-arrow (——→or⟶), its antarafacial use. This symbolism also provides the selection rule for the reaction with a *n*umber (x) of *f*ull arrows in the pericycle; pericyclic reactions with an odd Nf are allowed under thermal conditions and those with an even Nf are allowed under photochemical conditions.

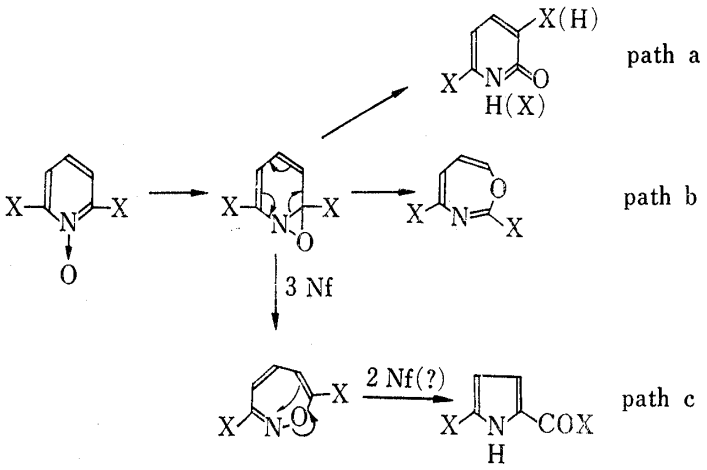


Chart 2. Photo-rearrangement Processes of Pyridine 1-Oxides

Photochemistry of tricyclic azine N-oxides is less thoroughly examined than those of mono- and bicyclic ones. Five isomers of tricyclic azine can be obtained regarding quinoline as the (theoretical) progenitor of this series.

9) O. Buchardt, B. Jensen, and I.K. Larsen, *Acta Chem. Scand.*, **21**, 1841 (1967).
10) C. Kaneko, S. Yamada, I. Yokoe, and M. Ishikawa, *Tetrahedron Letters*, **1967**, 1873.
11) P.L. Kumler and O. Buchardt, *Chem. Commun.*, **1968**, 1321.
12) Photo-rearrangement reactions of diazine N-oxides are, in general, not so different from those of the corresponding monoazine N-oxides.[4,5]
13) R.B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, 1970, p. 169.
14) C. Kaneko, *Tetrahedron*, **28**, 4915 (1972); *idem*, *Rep. Res. Inst. Med. Engi., Tokyo Medico-Dental Univ.*, **7**, 7 (1973); *idem*, *ibid.*, **8**, 1 (1974). See also reviews on this symbolism: C. Kaneko, H. Ichikawa, K. Shudo, and S. Tanaka, *Kagaku no Ryoiki*, **28**, 487, 562, 623, 717 (1974).

Thus, a benzene ring could be added to quinoline in five different annelation patterns, *viz.*, in the 2: 3 (=*b*)-position to give acridine, in the 3: 4 (=*c*)-position to give phenanthridine, and on three facets (*f*, *g*, and *h*) of the benzene ring to give the three benzoquinolines. The data available, though scanty, for the N-oxides of the last four benzologs of quinoline indicated that their photochemical behavior is essentially the same in the photo-isomerization reactions with that of quinoline 1-oxides.[15] On the contrary, at the outset of the present study, there was only one paper by Mantsch and Zanker[16] reporting the formation of solvent-addition products from acridine 10-oxide by irradiation in an alcoholic medium and these authors suggested quite a different mechanism for it from those given above including the initial formation of 9,10-epoxyacridine as a key intermediate.

This and the fact that acridine 10-oxide represents the simplest class of tricyclic N-oxides and their higher benzologs whose photochemistry has not been explored prompted us to examine the photochemistry of this N-oxide and its derivatives.

This paper reports the results of these experiments as well as mechanistic rationalizations of the photo-rearrangement reactions thus found.

Results of Irradiation Experiments

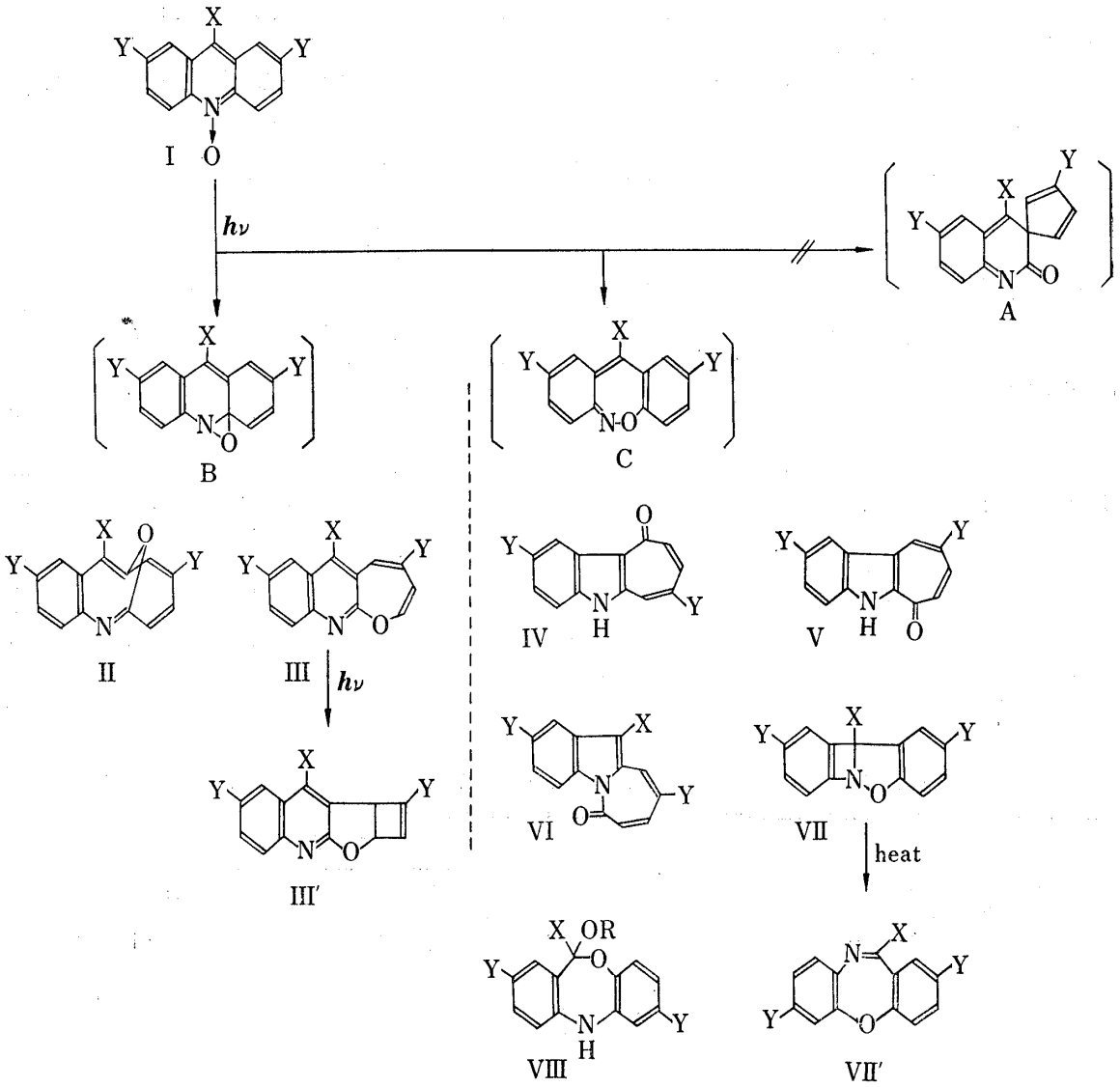
Acridine 10-oxides (Ia) and its substituted derivatives (Ib—Ig) were photolysed in a variety of solvents. Irradiation was made with a Hanovia high-pressure mercury arc lamp with a Pyrex filter. The reactions were monitored by periodical measurements of the ultraviolet (UV) spectra of the reaction mixture and terminated when almost all of the starting N-oxide was consumed. (In general, the irradiation period necessary for the reaction lies between 2 and 10 hr, if 1 g of the N-oxide in 600 ml of the solvent was irradiated by a 450-W lamp). After the irradiation, the solvent was evaporated under a reduced pressure and the residue was chromatographed over silica gel or alumina. As reminiscent of the photolysis of other class of aromatic amine oxides, the deoxygenation products (acridines) (IX) were obtained in these photolyses.[4,17] However, the yields were very low (1—3%). The products other than acridines are shown in Chart 3. Apparently, they were much more complex in number as well as in structure than those of bicyclic azine N-oxides (*e.g.*, quinoline 1-oxides, see Chart 1). As will be discussed later, these products can be classified into two groups, B and C (which correspond to the pathways, b and c, as proposed for those in the photo-rearrangements of mono- and bi-cyclic azine N-oxides) on the basis of the relative position of the substituents in the products as well as the solvent effect upon product distribution in these photolyses.

Products are classified a B group when their formation from the oxaziridine (B) can be explained by 1,5- or 1,9-oxygen rearrangement (note that 1,4n+1 suprafacial sigmatropic rearrangement is a thermally allowed pericyclic reaction; an odd Nf reaction). The products, II and III, belong to this group. The compounds III′ should also be included in this group since as mentioned in the experimentals, they were formed from III by the same irradiation as that employed for the photolysis of N-oxides (this process is a photochemically allowed process; a 2 Nf reaction).

15) Photolysis of phenanthridine 5-oxides: *a*) M. Ishikawa, S. Yamada, H. Hotta, and C. Kaneko, *Chem. Pharm. Bull.* (Tokyo), **14**, 1102 (1966); *b*) E.C. Taylor and G.G. Spence, *Chem. Commun.*, **1968**, 767, 1037. Photolysis of benzo[*f*]- and benzo[*g*]-quinoline 1-oxides: *c*) C. Kaneko, S. Hayashi, and M. Ishikawa, *Rep. Res. Inst. Med. Engi., Tokyo Medico-Dental Univ.*, **4**, 149 (1970). Photolysis of benzo[*h*]-quinoline N-oxide in a hydroxylic solvent afforded the corresponding 2-oxo compound: Unpublished result from this laboratory (by C.K. and S.Y.).

16) H. Mantsch and V. Zanker, *Tetrahedron Letters.*, **1966**, 4211; H. Mantsch, V. Zanker, W. Seiffert, and G. Prell, *Liebigs Ann. Chem.*, **723**, 95 (1969).

17) It is now generally believed that the lowest triplet state (π,π^*) of the N-oxide is responsible for the deoxygenation, while the singlet state is responsible for the isomerization (oxaziridine formation): *a*) I. Ono and N. Hata, *Bull. Chem. Soc. Japan*, **46**, 3658 (1973); *b*) N. Hata, I. Ono, and M. Kawasaki, *Chem. Lett.*, **1975**, 25.



	a	b	c	d	e	f	g
X	H	H	CH_3	CH_3	CH_2CH_3	CN	CN
Y	H	CH_3	H	CH_3	CH_3	H	CH_3

Chart 3

Other products, IV-VII, are classified into C group. The presence of a substituent at 9-position of the N-oxide (I) precludes the formation of IV and V. The formation of these products can be explained as being formed *via* the 1,2-oxazepine (C), the valence-bond tautomer of the oxaziridine (B). In the photolysis of these N-oxides unsubstituted at the 9-position in a hydroxylic solvent, the solvent-addition products (VIII) were obtained in some cases which we also placed in the C-type product for the reason to be mentioned later. Differing to the simple oxygen rearrangement products (II, III, and III′), the relative position of the substituents in the C-type products may not necessarily be the same with that in the starting N-oxides.

There seemed to be no products which might have been formed *via* path a. Thus, in these photolyses, product expected from the cyclopentadiene intermediate (A in Chart 3) was not

detected.[18] This fact is in good accordance with the afore-mentioned discussions that this path is thermal in nature.

Tables I and II summarize the products and their distribution obtained in a variety of solvent systems.

Table I. Irradiation Products of 9-Unsubstituted Acridine 10-Oxides

Acridine 10-oxide I (X=H)	Solvent	Yield (%)					
		class B		class C			
		II	III (III')	IV	V	VI	VIII
Ia (Y=H)	benzene	—	—	32	20	5	—
	CH_3OH	—	—	—	—	—	80
	CH_2Cl_2	—	—	70	—	—	—
	aq. CH_3CN[a]	12	30	3	—	—	—
Ib (Y=CH_3)	benzene	6—9	8—13	5—13	18—40	2—4	—
	CH_2Cl_2	—	3	56	3	—	—
	CH_3CN	12	15	5	22	1	—
	C_2H_5OH	21	25	25	1	1	—
	CH_3OH	19	50	—	—	—	5
	aq. CH_3OH[a]	16	60	—	—	—	1

a) 1:1 v/v.

Table II. Irradiation Products of 9-Substituted Acridine 10-Oxides

Acridine 10-oxide I (X≠H)		Solvent	Yield (%)			
			class B		class C	
			II	III (III')	VI	VII (VII')
Ic	X=CH_3, Y=H	benzene	—	—	7[a]	15[a]
Id	X=CH_3, Y=CH_3	benzene	2	10	33	7
		CH_2Cl_2	14	40	—	—
		CH_3OH	15	56	2	—
Ie	X=CH_2CH_3, Y=CH_3	benzene	3	20	39	—
		CH_3OH	16	60	—	—
If	X=CN, Y=H	benzene	2	25	10	—
Ig	X=CN, Y=CH_3	benzene	3	19	3	—
		aq. CH_3CN[b]	1	50	—	—

a) an appreciable amount of the starting N-oxide was recovered.
b) 1:1 v/v.

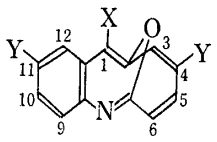
Determination of the Structure of Photo-products

Since the relative position of the substituents in the photo-products may either be changed (in C-type products) or unchanged (in B-type products) from that of the starting N-oxides and the mechanism clarified in the present study depends largely on this fact, the structure determination of the products required a more thorough experiment if substituents were present in the starting N-oxides.

18) In the dienone-phenol rearrangements (typical acid-catalyzed thermal reactions), product as expected from the cyclopentadiene intermediate such as A was not obtained. See N.L. Wandler, "Molecular Rearrangements," ed. by P. deMayo, Interscience Publ. Co., New York, Vol. 2, 1028 (1964), and references cited therein.

Benz[*c*]-2-aza-1,6-oxido[10]annulenes (II)——The spectroscopic data are shown in Table III. In their infrared (IR) spectra, these compounds showed no absorption bands due to carbonyl or hydroxyl group. The UV spectra of these products are not so different from those

TABLE III. Spectroscopic Data of II



Compound	ν_{max}^{KBr} (cm^{-1})	$\lambda_{max}^{95\%EtOH}$ nm (log ε)	NMR τ *J* in Hz a: $CDCl_3$ b: benzene-d_6								
			solv.	X	H_3	Y_4	H_5	H_6	H_9	H_{10}	Y_{11}	H_{12}
IIa	1560	267(4.73)	a	2.2—2.8		3.15	2.2—	2.9	2.0	2.2—2.8		2.08
	1130	356(3.74)		m		d, d	2.8	d	d	m		d
						10, 9	1.0, 9	8	8			
	880		b	3.2	2.6—	3.7	3.4	3.05	1.89	2.6—2.9		2.45
	765			s	2.9	d, d	d, d	d	d	m		d
					m	10, 9	10, 9	1.0	8			8
IIb	1568	272(4.77)	a	2.70	2.70	7.62	3.0	2.7	2.08	2.45	7.50	2.30
	1150	363(3.77)		s	s	s	d	d	d	d	s	s
							11	11	8	8		
IId	1570	275(4.55)	a	7.60	2.60	7.60	3.03	2.75	2.1	2.49	7.48	2.16
	1150	368(3.58)		s	s	s	d	d	d	d	s	s
							11	11	8	8		
	828		b	8.0	2.97	8.0	3.5	2.95	1.98	2.78	7.7	2.4
				s	s	s	d	d	d	d	s	s
							11	11	9	9		
IIe	1570	276(4.69)	a	9.07	2.6	7.6	3.0	2.8	2.12	2.48	7.47	2.12
	1150	370(3.80)		t, 8	s	s	d	d	d	d	s	s
	825			6.9-7.3			11	11	8	8		
				m								
IIf	2220	276(4.65)	a	—		2.1—3.0			2.0	2.1—3.0		1.75
	1570	375(3.89)				m			d	m		d
	1140								8			8
IIg	2220	282.5(4.64)	a	—	2.43	7.53	2.95	2.71	2.08	2.39	7.42	1.96
	1570	385(3.91)			s	s	d	d	d	d	s	s
	1145						11	11	8	8		

of the corresponding acridines (IX). In their NMR spectra, the signals of the ring protons and methyl groups appeared in the region of aromatic ones. This fact shows that the products (II) are a novel class of aromatic compounds; aza analogs of 1,6-oxido[10]annulene.[19] Further confirmation of the structure of II has been provided by the following chemical reactions. Catalytic hydrogenation of IIb in methanol over palladium on charcoal afforded 2,7-dimethylacridine (IXb) and the tetrahydrocyclohept[*b*]indol-10-one (Xb) in respective yields of 15 and 37%. Refluxing of IIb in benzene in the presence of BF_3-etherate yielded IXb and 2,7-dimethylacridin-4-ol (XIb) in 1: 2 ratio. Structure of the acridinol (XIb) was supported by the similarity of its UV spectrum with that of an authentic 4-acridinol[20] (XIa). The position of methyl groups in the rearrangement products (Xb and XIb) was unequivocally determined from their nuclear magnetic resonance (NMR) spectrum.

19) *a*) E. Vogel, M. Biskup, W. Pretzer, and W.A. Boll, *Angew. Chem.*, **76**, 785 (1964); *b*) F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, **86**, 3168 (1964); *c*) A. Shani and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 6310 (1967).

20) A. Albert and P. Short, *J. Chem. Soc.*, **1945**, 760.

Deoxygenation to acridine as well as isomerization to the acridinol in these reactions are closely related to the reactions of 1,6-oxido[10]annulene.[19] By analogy, these reactions may be considered to proceed *via* the epoxyacridine intermediate (D) (Chart 4). The same type

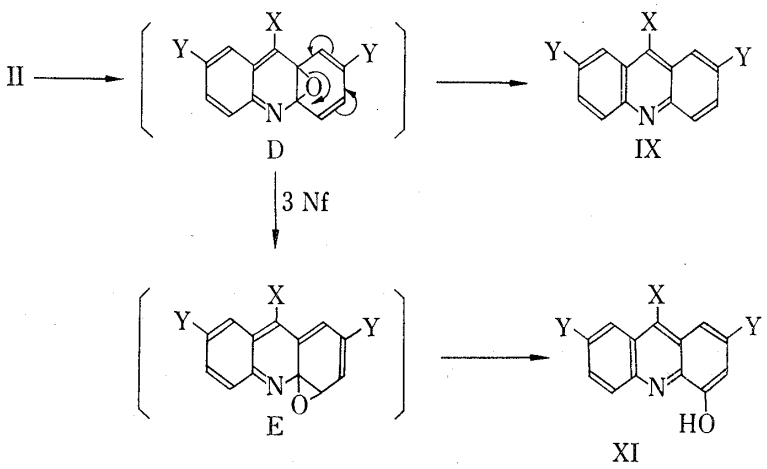
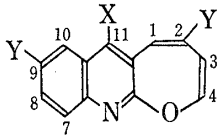


Chart 4

of rearrangement reactions has also been found to occur in 3,1-benzoxazepines[21] under a comparable condition.

Oxepino[2,3-*b*]quinolines (III) and 2a,9b-dihydrocyclobuta[4,5]furo[2,3-*b*]quinolines (III′)——The NMR spectra of III and III′ are shown in Table IV. The spectrum of III indi-

Table IVa. NMR Spectral Data of III[a]

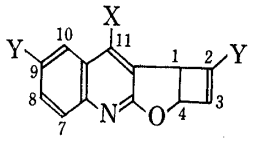


Compd.	NMR τ ($CDCl_3$) J in Hz								
	H_1	Y_2	H_3	H_4	H_7	H_8	Y_9	H_{10}	X
IIIa	3.37	3.95	4.45	3.55		2.1—2.5			
	d	d, d	t	d		m			
	12	12, 6	6	6					
IIIb	3.60	8.0	4.58	3.58	2.22	2.56	7.5	2.53	2.33
	s	s	d	d	d	d, d	s	s	s
			6	6	8	8, 2			
IIId	3.30	7.95	4.43	3.48	2.23	2.55	7.48	2.28	7.38
	s	s	d	d	d	d, d	s	s	s
			6	6	8	8, 2			
IIIe	3.30	7.95	4.42	3.45	2.18	2.53	7.45	2.25	8.72
	s	s	d	d	d	d, d	s	s	t, 8
			6	6	8	8, 2			6.88
									q, 8
IIIf	3.0	3.67	4.33	3.51		1.8—2.5			—
	d	d, d	t	d		m			
	12	12, 6	6	6					
IIIg	3.15	7.95	4.40	3.50	2.15	2.43	7.48	2.13	—
	s	s	d	d	d	d, d	s	s	
			6	6	8	8, 2			

a) UV and IR: see Ph. D. Thesis of S. Yamada, Tokyo University, Faculty of Pharmaceutical Science (1975).

21) S. Yamada and C. Kaneko, *Rep. Res. Inst. Med. Engi., Tokyo Medico-Dental Univ.*, **3**, 75 (1969). See also, C. Kaneko and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), **15**, 663 (1967).

TABLE IVb. NMR Spectra of III′[a)]

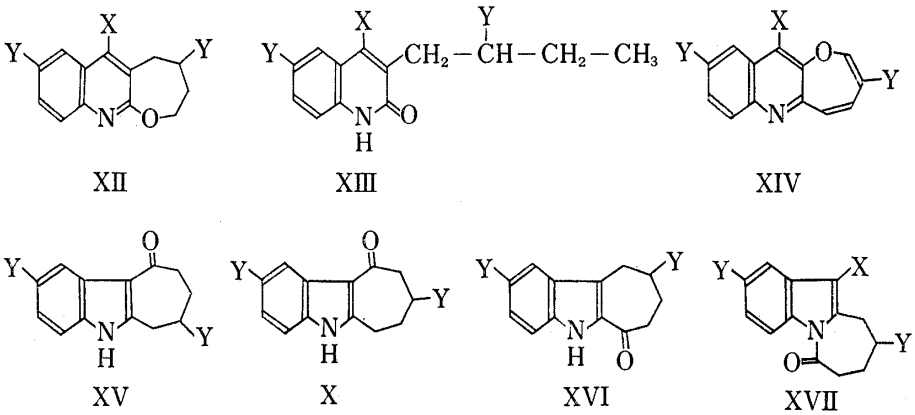


Compd.	NMR τ ($CDCl_3$) J in Hz								
	H_1	Y_2	H_3	H_4	H_7	H_8	Y_9	H_{10}	X
III′b	5.7	8.15	4.1	4.55	2.25	2.6	7.5	2.53	2.2
	m	s	m	m	d	d	s	s	s
	b				8	8			
III′c	5.5	3.40	3.78	4.43		2.1—2.65			7.45
	d	t	d	t		m			s
	3	3	3	3					
III′d	5.6	8.15	4.05	4.55	2.25	2.57	7.5	2.38	7.4
	m	s	m	m	d	d, d	s	s	s
					8	8, 2			
III′e	5.6	8.15	4.0	4.53	2.22	2.57	7.5	2.33	8.65
	d	s	s	d	d	d, d	s	s	t, 7
	2.5			2.5	8	8, 2			7.0m
III′f	5.26	3.30	3.69	4.28		1.9—2.6			—
	d	t	d	t		m			
	3	3	3	3					
III′g	5.38	8.00	3.99	4.40	2.19	2.46	7.43	2.23	—
	d, d	s	s	d	d	d, d	s	s	
	2.5, 1			2.5	9	9, 2			

a) UV and IR: see Ph. D. Thesis of S. Yamada, Tokyo University, Faculty of Pharmaceutical Science (1975).

cates clearly that these have an oxepine ring, since the pattern of the signals in the olefinic region resembles quite closely that of benz[*b*]oxazepine.[19c)]

Catalytic hydrogenation of III gave two products (XII and XIII). Thus, for example, the reduction of IIIb afforded XIIb (38%) whose UV spectrum resembles that of quinoline itself and XIIIb (31%). The UV and IR spectra (KBr; 1650—1660 cm^{-1}) of XIIIb show the presence of carbostyril chromophore in it.[22)] The formation of XIIIb in this experiment excludes definitely the alternative oxepine structure; oxepino[3,2-*b*]quinoline system (XIV) for III.



XII XIII XIV

XV X XVI XVII

Chart 5

22) The reductive C-O bond fission as observed in the formation of XIII is similar to the formation of 4-methoxy-3-ethylcarbostyril from dictamine under a comparable condition. See T. Ohta, *Yakugaku Zasshi*, **73**, 63 (1953).

Since these compounds (III) gave III′ in nearly quantitative yields by irradiation (under identical conditions with the photolysis of I) in an appropriate solvent (ethanol, methanol, *etc.*), the structure of III′ was also confirmed. The common presence of 2a, 9b-dihydrocyclobuta[4,5]furo[2,3-*b*]quinoline skeleton in III′ is also supported by the comparison of their NMR spectra with that of 2-oxabicyclo[3.2.0]hept-6-ene.[23]

Cyclohept[*b*]indol-10(5H)-ones (IV)——These compounds were obtained by photolysis of acridine 10-oxides having no substituent at 9-position. Like II, III, and III′, they have the same molecular composition as the starting N-oxides. Some of the properties of IV are shown in Table V.

TABLE V. Spectroscopic Properties of IV

Compd.	ν_{max}^{KBr} (cm^{-1})	$\lambda_{max}^{95\%EtOH}$ nm (log ε)[a]	NMR (τ) a: $(CD_3)_2SO$ J in Hz b:CF_3COOH
IVa	2700—3060	218 (4.55)	a) 2.2—3.0 m 7H,
	1550	237 (4.42)	1.2 d (J=8) 1H,
	1515	281 (4.37)	−2.35 broad s 1H
	1480	362 (3.92, sh.)	
		376 (4.01)	
		396 (3.91)	
IVb	2800—3200	221 (4.57)	b) 7.30 s 3H, 7.08 s 3H,
	1550	241 (4.44)	2.22 s 2H, 2.00 d (J=13) 1H,
	1520	302 (4.39)	1.83 d (J=13) 1H
	1485	382 (3.98)	1.50 s 1H, 1.37 s 1H,

a) UV spectra of IVa in 5% KOH and 1 N HCl were reported in ref. 2a.

The compound (IVa) afforded the tetrahydro compound (XVa) by catalytic hydrogenation. This product was identified with 6,7,8,9-tetrahydrocyclohept[*b*]indol-10(5H)-one obtained in our earlier study.[24] This fact and the spectral data (the UV spectra of IVa in neutral, acidic, and basic media were reported and discussed in detail earlier[2a]) decomstrate clearly that IVa and IVb have cyclohept[*b*]indol-10(5H)-one as their common skeleton.

The position of two methyl groups in IVb and its terahydro derivative (XVb), obtained by catalytic hydrogenation of IVb, was deduced as at the 2- and 7-positions in the cycloheptindolone skeleton from the analysis of their NMR spectra (the detailed analysis of the spectra was reported in one of the earlier papers of this series[2c]). Further, the tetrahydro compound (XVb) obtained from IVb was different from tetrahydro compound (Xb) obtained from IIb. As mentioned, structure of the latter compound (Xb) was determined as 2,8-dimethyl-6,7,8,9-tetrahydrocyclohept[*b*]indol-10(5H)-one.

Cyclohept[*b*]indol-6(5H)-ones (V)——As shown in Table VI, the spectroscopic properties of Va and Vb somewhat resembled those of IV. By catalytic hydrogenation, Vb was converted to the tetrahydro compound (XVIb) having a UV absorption typical to 2-acylindoles. This experiment demonstrated that the tetrahydro derivatives of V have 7,8,9,10-tetrahydrocyclohept[*b*]indol-6(5H)-one skeleton and thus their parents should have the structures as assigned. Very recently, de Jong, *et al.*[25] synthesized Va and confirmed the identity of their sample with ours by the mixed melting point determination.

The position of the methyl groups in Vb was determined from the examination of the ring proton region in its NMR spectrum. The fine splitting of the high-field doublets and the appearence of a singlet at a lower field due to the protons on the seven-membered ring indicated the presence of the 4-methyl-2,4-dienone function.

23) L.A. Paquette, J.H. Barrett, R.P. Spitz, and R. Pitcher, *J. Am. Chem. Soc.*, **87**, 3417 (1965).
24) C. Kaneko, I. Yokoe, S. Yamada, and M. Ishikawa, *Chem. Pharm. Bull.* (Tokyo), **17**, 1290 (1969).
25) One of the present authors (C.K.) thanks Prof. de Jong for his kind performance of the determination; J. de Jong and J.H. Boyer, *J. Org. Chem.*, **37**, 3571 (1972).

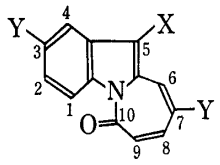
TABLE VI. Spectroscopic Data of V

Compd.	ν_{max}^{KBr} cm^{-1}	$\lambda_{max}^{95\%EtOH}$ nm (log ε)	NMRλ in a, $(CD_3)_2SO$; b, CF_3COOH (J in Hz)
Va	3200 1615 1565 1555	224 (4.47), 276 (4.46), 309 (4.30), 320 (4.29), 336 (4.17), 383 (3.92), 403 (4.03)	b) 1.35—2.3 m (7H) 0.55 d (10) (1H)
Vb	3200 1625 1550 1490	230 (4.43) 273 (4.30) 280 (4.31) 327 (4.27) 410 (3.89)	a) 7.5 s (6H), 2.83 d (13) (1H), 2.45 d(13) (1H), 2.57 d(8) (1H) 2.35 d(8) (1H), 1.88 s (1H), 1.78 s (1H), -2.33 s (1H) b) 7.33 s (3H), 7.0 s (3H), 2.20 s (2H), 1.88 d(12) (1H), 1.73 s (1H), 1.65 d(12) (1H), 0.73 s (1H)

10-Oxo-10H-azepino[1,2-*a*]indoles (VI)——These compounds were obtained as main products in the photolysis of 9-substituted acridine 10-oxides in a nonpolar solvent. However, their yields decreased appreciably in the photolysis of 9-unsubstituted N-oxides. By catalytic hydrogenation, these compounds afforded the corresponding tetrahydro compounds (XVII) showing UV and IR (carbonyl bands) spectra typical of N-acylindoles.

From these facts, 6,7,8,9-tetrahydro-10-oxo-10H-azepino[1,2-*a*]indole structure for XVII and 10-oxo-10H-azepino[1,2-*a*]indole structure for VI are deduced. The identity of XVIIa with the authentic sample obtained in our earlier study[24] further confirmed this conclusion. The position of the substituent in these compounds (VI) was determined from their NMR

TABLE VIIa. NMR Spectral Data of VI[a]



Compd.	NMR τ ($CDCl_3$) J in Hz								
	H_1	H_2	Y_3	H_4	X	H_6	Y_7	H_8	H_9
VIb	1.13 d 8	2.71 d, d 8, 2	7.50 s	2.52 s	3.16 s	2.94 s	7.8 s	3.28 d, d 13, 2	3.58 d 13
VIc	1.6 m		2.2—2.65 m		7.5 s	2.2— 2.65 m	3.8 d, d 13, 8	3.18 d, d 13, 8	3.58 d 13
VId	1.10 d 8	2.67 d, d 8, 2	7.50 s	2.54 s	7.60 s	2.88 s	7.8 s	3.28 d, d 13, 2	3.62 d 13
VIe	1.09 d 8	2.67 d, d 8, 2	7.45 s	2.5 s	8.7 t, 8 7.05 q, 8	2.87 s	7.75 s	3.28 d, d 13, 2	3.60 d 13
VIf	1.05 d, d 7, 3		2.1—2.5 m		—		2.8—3.5 m		
VIg	1.25 d 9	2.62 d, d 9, 2	7.45 s	2.41 s	—	2.65 s	7.65 s	3.15 d, d 13, 2	3.40 d 13

a) The spectrum of VIa could not be analyzed.

spectra. For example, two sets of doublets at 3.28 and 3.58 τ(J=13 Hz) in the spectrum of VIb indicated the presence of 4-methyl-2,4-dienone function in the seven-membered ring. Table VII shows the NMR spectra of these azepinoindoles (VI).

Table VIIb. UV and IR Spectra of VI

Compd.	ν_{max}^{KBr} : cm^{-1}	λ_{max} : nm (log ε) a : 95% EtOH b : CH_2Cl_2
VIa	1660	a 284
	1630	428
	805	
VIb	1665	a 258 (4.29), 291 (4.54)
	1630	430 (3.45)
VIc	1676	b 288 (4.46), 310 sh. (4.14)
	1655	440 (3.49)
	1626	
VId	1660	a 263 sh. (4.24), 293 (4.57)
	1630	450 (3.42)
VIe	1660	a 259 sh. (4.37), 292.5 (4.71)
	1630	444 (3.65)
VIf	2220	b 256 (4.04), 284.5 (4.18)
	1668	312 (4.11), 415 (3.59)
	1630	
VIg	2215	b 263 (4.16), 293 (4.37),
	1674	316 (4.36), 415 (3.76)
	1640	

Dibenz[*c*,*f*]-2-oxa-1-azabicyclo[3.2.0]hepta-3,6-dienes (VII)——Only two acridine 10-oxides having a methyl group at 9-position (Ic and Id) gave the corresponding VII-type compounds. The compound VIIc was obtained from the irradiation mixture of Ic by alumina column chromatography. This compound is quite readily isomerized to VII'c. For example, silica gel chromatography of VIIc by an ordinary organic solvent afforded VII'c in a quantitative yield. Therefore, in order to obtain this type of compounds (VII), the irradiation products should be separated by alumina column chromatography. The NMR spectrum of VIIc in $CDCl_3$ also changed gradually and after two days from its preparation at room temperature, the spectrum of the solution became identical with that of VII'c. The spectra of VII and VII' are shown in Table VIII (the product from Id was obtained as VII'd). Since physical properties of the rearrangement product (VII'c) seemed to be quite similar to those of dibenz-

Table VIII. Spectral Data of VII and VII'

Compd.	ν_{max}^{KBr} : cm^{-1}	$\lambda_{max}^{95\%EtOH}$: nm (log ε)	NMR τ ($CDCl_3$) methyl	ring protons
VIIc	1215	292 (3.72)	8.0 s	3.0—3.4 m (2H)
	755	330 sh (2.61)	(3H)	2.7—2.95 m (6H)
VII'c	1620	221 sh (4.32)	7.4 s	2.5—2.95 m (8H)
	1205	256 sh (3.77)	(3H)	
	795	292 (3.62)		
	760	318 (3.61)		
VII'd	1620	226 (4.46)	7.68 s (6H)	2.8—3.2 m (6H)
	1490	302 (3.75)	7.45 s (3H)	
	1210	322 (3.73)		
	830			

[*b*,*f*][1,4]oxazepine (VII′: X=Y=H), reported by Higginbottom and Suschitzky,[26] we have prepared several methyl derivatives of it according to their method. Two of them prepared as shown in Chart 6 were identified with VII′c and VII′d, respectively. From this fact and from the spectroscopic data of VIIc, we assigned VII-structure to these labile photo-products. A tentative mechanism for the rearrangement from VII to VII′ is shown in Chart 7. As will be mentioned later, the formation of products having the structure VII is in good accordance with the proposed photo-rearrangement scheme for acridine 10-oxides (*c.f.*, Chart 9; the conversion of C to VII is a 2Nf reaction and thus must be photochemical, if it proceeds concertedly).

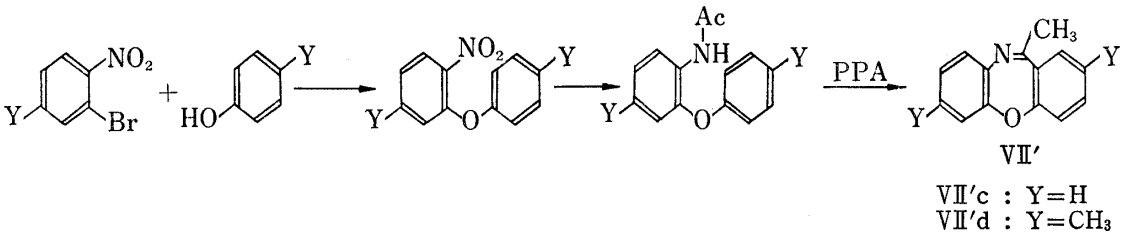


Chart 6

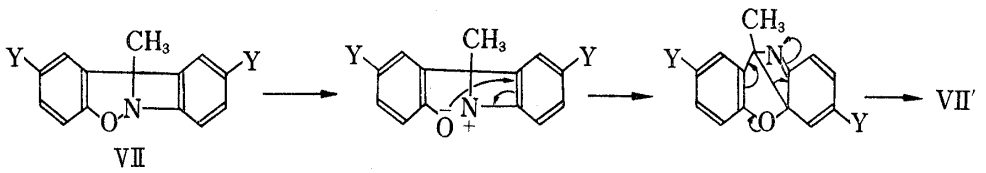


Chart 7

11-Alkoxy-5,11-dihydrodibenz[*b*,*e*][1,4]oxazepines (VIII)——The compounds (VIII) were obtained only from 9-unsubstituted acridine 10-oxides by irradiation in an alcoholic solvent. From elemental compositions and mass and NMR spectra, it becomes apparent that these are formed by addition of the alcohol (1 mol. eq.) used as a solvent to the N-oxides.

Table IX. UV and NMR Spectral Data of VIII

Compd.	R	$\lambda_{max}^{95\%\ EtOH}$: nm (log ε)	solv.	NMR τ (J in Hz) a : $CDCl_3$ b : CCl_4
VIIIa	CH_3	290 (4.35)	a	6.4 s (3H), 4.23 s (1H), 2.6—3.35 m (8H)
VIIIa	CH_2CH_3	290 (4.30)	b	8.8 t (8) (3H), 6.4 q (8) (2H), 4.28 s (1H), 2.45—3.5 m (8H)
VIIIb	CH_3	292 (4.40)	a	7.75 s (6H), 6.38 s (3H), 4.25 s (1H), 3.43 s (1H), 3.37 d (8) (2H), 3.03 d (8) (1H), 2.98 d (8) (1H), 2.83 s (1H)

The compounds (VIII) were sensitive to an acidic condition (such as chromatography over silica gel, diluted hydrochloric acid at room temperature, *etc.*), and gave the corresponding phenol aldehydes (XIX) which cyclized to acridinols (XX) in a quantitative yield by boiling in diluted hydrochloric acid. Very interestingly, the acridinol (XXb) obtained from VIIIb is different from XIb obtained from IIb by a Lewis acid (*vide supra*). This fact and the almost identical UV and IR spectra of the two samples indicate that these two compounds (XXb and XIb) are the isomers differing only in the position of the methyl groups. The pres-

26) R. Higginbottom and H. Suschitzky, *J. Chem. Soc.*, **1962**, 2367.

ence of two vicinal protons on the phenol ring (2.93 and 2.75 τ, each as a doublet with $J=7$ Hz) in XXb was clearly demonstrated by the large coupling constant (7 Hz). Hence XXb was determined as 1,7-dimethylacridin-4-ol. From this fact, it is concluded that the solvent-addition product (VIIIb) derived from Ib must be 2,7-dimethyl-11-methoxy-5,11-dihydrodibenz[*b*,*e*][1,4]oxazepine. Reactions of VIII so far carried out are shown in Chart 8.

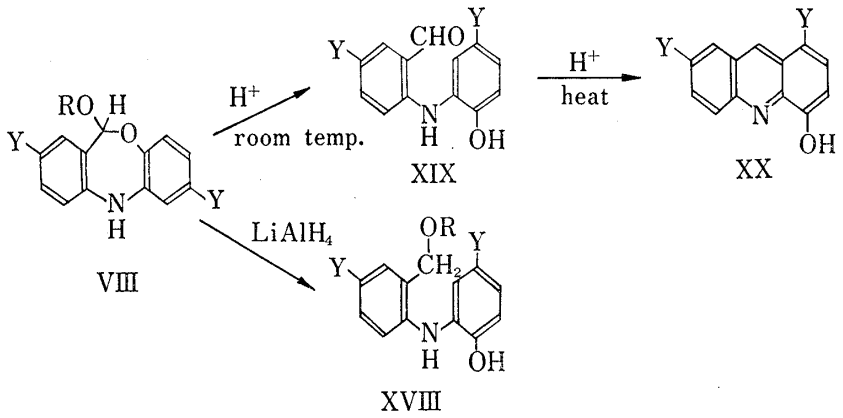


Chart 8

Discussions

From the solvent effect on the product distribution (Tables I and II) and on the basis of the structure of each photo-product, it seems reasonable to divide the photo-products of acridine 10-oxides into two groups (B and C as shown in Chart 3), except the solvent-addition products (VIII) which are formed only in methanol or ethanol. According to this classification, the following might be concluded from the data obtained in the present study: (i) The formation of B-product (II, III, and III') was preferred in a polar medium (*e.g.*, methanol), while that of C-products predominated in a nonpolar medium (*e.g.*, benzene) and (ii) position of the methyl groups in C-products could be reasonably explained only if we consider the participation of the spiro-intermediates (*e.g.*, F and H). The mechanism accounting for all of them is shown in Chart 9.

The oxaziridine (B) formed from the photo-excited N-oxide (I) equilibrates with its valence-bond tautomer, the 1,2-oxazepine (C). The former species predominates over the other species in a polar medium, while the latter species predominates over the other species in a nonpolar solvent. In accordance with this assumption, it is well known that the proportion of benzene-oxide increases with increasing dielectric constant of solvent in benzene-oxide⇄oxepine equilibrium.[27] This equilibrium process as well as that of B⇄C are of course thermally allowed (3 Nf) pericyclic reactions.[13,14]

The former species (B) afforded the B-products by 1,5- or 1,9-oxygen shift (these are 3 Nf and 5 Nf processes and thus again thermally allowed). Hence, by this pathway, the position of the substituents does not change throughout the reaction as verified by the above experiments.

The latter species (C) rearranges to the spiro compound (F) which in turn affords the C-products by subsequent C–C bond fission and recyclization. The almost exclusive formation of the solvent addition product (VIIIa) from Ia by irradiation in methanol[16] necessarily suggests that the addition of methanol should occur at the equilibration stage (B⇄C) to C-species, because otherwise (*e.g.*, addition of methanol to F-species, *etc.*) the high polarity of the solvent should have increased the yield of the B-products.

27) E. Vogel and H. Gunther, *Angew. Chem. Int. Ed.*, **6**, 385 (1967).

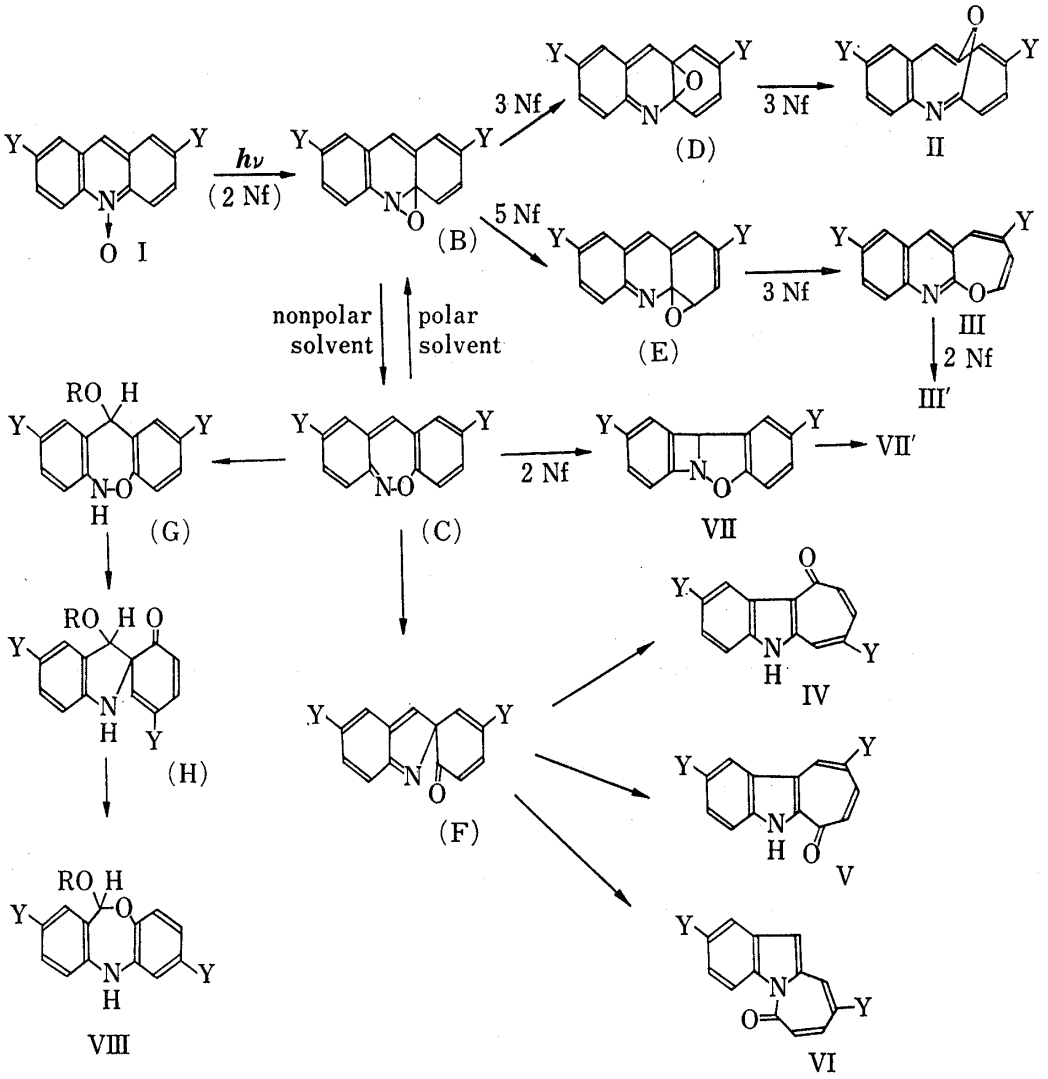


Chart 9. Photo-rearrangement Pathways of Acridine 10-Oxides
2,7-Substituted one is chosen as a model.

Two mechanisms different from ours have been proposed by other researchers[16,28] including one 1,5-shift of oxygen atom from the 9,10-epoxyacridine or the two successive 1,5-oxygen shifts from the oxaziridine (B). It should be noted that neither of them can explain the positional change of the methyl groups between 2,7-dimethylacridine 10-oxide (Ib) and its solvent-addition product (VIIIb). The isolation and identification of VII also seem to support the present mechanism, since such products can be formed from C-species by 2 Nf process (and thus by irradiation).

We will report later[29] the direct isolation of two dibenz[*c*,*f*][1,2]oxazepines (C-species) by the photolysis of 9-cyano- and 9-chloro-acridine 10-oxides and clarify the nature (thermal or photochemical) of all the reaction pathways leading to the C-products.

Experimental

The melting points were determined in a capillary tube and are uncorrected. The UV spectra were measured on a Hitachi Model-323 spectrometer. The NMR spectra were obtained using a C-60 HL-JEOL

28) p. 261 of Reference 4*c*.
29) S. Yamada and C. Kaneko, unpublished data. A part of this study appeared as a communication: *J. Chem. Soc., Chem. Commun.*, **1972**, 1093.
30) The photo-reactions of phenazine 5-oxide and its higher benzologs have been reported: *a*) A. Albini, G.F. Bettinetti, and S. Pietra, Tetrahedron Letters, **1972**, 3657; *b*) C. Kaneko, S. Yamada, and M. Ishikawa, *Tetrahedron Letters.*, **1970**, 2329.

(60 Mcps) spectrometer and the chemical shifts are in τ-units. The mass spectra were obtained on a Hitachi Model-RMU-7M double focus mass spectrometer using in all cases a direct sample insertion into the ion source. All the new compounds described in this paper are supported either by satisfactory analytical results or by the presence of the corresponding parent peaks in the mass spectra.

Acridine 10-Oxides (Ia—Ig)——All the acridine 10-oxides were prepared from the corresponding acridines by oxidation with *m*-chloroperbenzoic acid (1 mol. eq.) in benzene or $CHCl_3$. After being kept standing over night at room temperature, the reaction mixture was shaken in 10% KOH solution and the organic layer was dried over $MgSO_4$. Evaporation of the solvent followed by recrystallization of the residue from Me_2CO–CH_2Cl_2 gave the N-oxides. The yields were 70—85%. Table X shows their mp's.

Table X. Melting points of Acridine 10-oxides

Compd.	Ia	Ib	Ic	Id	Ie	If	Ig
mp (°C)	165—167	183—185	181—182 (decomp.)	210 (decomp.)	197—198	205—206 (decomp.)	211 (decomp.)

Irradiation of Acridine 10-Oxides——The N-oxide (I) was dissolved in 600 ml of the solvent. The solution was irradiated by Hanovia high pressure mercury arc lamp with a Pyrex filter. The reaction was monitored periodically by measuring the UV spectra (in 95% EtOH) of the reaction mixture and terminated when almost all of the N-oxide was consumed. After the reaction, the solvent was evaporated under a reduced pressure. If the starting N-oxide is the 9-unsubstituted ones, the residue was dissolved in acetone so as to remove insoluble products (IV and V). These products were then separated by fractional recrystallization from MeOH. In general, IV is less soluble than V in MeOH. The portion soluble to acetone was then purified by column chromatography. The photo-products obtained from 9-substituted N-oxides can be directly purified by column chromatography.

For chromatography, silica gel or alumina was used, but alumina must be used if the reaction products contain either VII or VIII. Table XI shows the elemental compositions of the photo-products.

Catalytic Hydrogenation of 4,11-Dimethylbenz[*c*]-2-aza-1,6-oxido[10]annulene (IIb)——IIb (95 mg) was dissolved in 50 ml of MeOH and the solution was hydrogenated at room temperature in the presence of 5% Pd/C (50 mg). After hydrogen take up was terminated (*ca.* 20 ml of H_2 was absorbed), the whole was filtered, the filtrate was concentrated, and the residue was recrystallized from acetone to give 35 mg of Xb, mp 290—295°. *Anal.* Calcd. for $C_{15}H_{17}ON$: C, 79.26; H, 7.54, N; 6.16. Found: C, 79.62; H, 7.48; N, 6.34.

The mother liquor was chromatographed over silica gel to give 14 mg of 2,7-dimethylacridine.

Reaction of IIb with BF_3-etherate in Benzene——To a solution of 95 mg of IIb dissolved in 20 ml of benzene, 10 drops of BF_3-etherate (this caused precipitation of the adduct which reverted to IIb by treatment with aq. alkali) were added and the whole was refluxed for 24 hr. The residue obtained by evaporation was made alkaline by adding Na_2CO_3 solution and extracted with $CHCl_3$. Chromatography of the residue obtained after evaporation of the solvent over silica gel gave 19 mg of 2,7-dimethylacridine and 38 mg of 2,7-dimethylacridin-4-ol (XIb), mp 172—175°. *Anal.* Calcd. for $C_{15}H_{13}ON$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.76; H, 5.82; N, 6.40. UV $\lambda_{max}^{95\%EtOH}$ nm: 264.5, 348, 366, and 390 (sh). NMR ($CDCl_3$): 7.52 s (CH_3), 7.47 s (CH_3), 3.0 s (1H), 2.80 s (1H), 2.47 d (J=9 Hz) (1H), 2.38 s (1H), 1.96 d (J=9 Hz) (1H).

Catalytic Hydrogenation of 2,9-Dimethyloxepino[2,3-*b*]quinoline (IIIb)——IIIb (160 mg) was hydrogenated in 50 ml of EtOH in the presence of 5% Pd/C (50 mg) at room temperature. After the hydrogen absorption terminated (*ca.* 45 ml), the catalyst was removed by filtration. Evaporation of the filtrate followed by chromatography of the residue over Al_2O_3 gave 61 mg of the tetrahydro compound (XIIb), mp 151—152° (ether); *m/e* 227 (M^+), 192, 172. UV $\lambda_{max}^{95\%EtOH}$ nm (log ε): 213 (4.71), 229 (4.54), 236 (4.54), 268 (3.65), 276 (3.65), 310 (3.67), 315 (3.66), and 323 (3.77). Its NMR spectrum is in good agreement with the proposed structure. As a more polar product, the carbostyril (XIIIb) was also obtained (50 mg), mp 123—124° (ether–hexane); *m/e* 229 (M^+) 214, 212, 200, 173. IR ν_{max}^{KBr} cm^{-1}: 1650 and 820. UV $\lambda_{max}^{95\%EtOH}$ nm (log ε): 216 (4.53), 231 (4.60), 233 (4.60), 273 (4.0), 281 sh (3.93), 333 (3.95), and 346 (3.81). The NMR spectrum of XIIIb was also in accordance with the proposed structure.

Catalytic Hydrogenation of 11-Cyanooxepino[2,3-*b*]quinoline (IIIf)——By the identical hydrogenation, 160 mg of IIIf afforded 35 mg of the tetrahydro compound (XIIf), mp 110—113.5° (ether–hexane); *m/e* 224 (M^+) and the carbostyril (XIIIf), 185—187 (acetone), *m/e*: 226 (M^+). The UV spectra of these are reported in our previous communications.[2b]

Irradiation of Oxepino[2,3,*b*]quinolines (III)——The solution of 100 mg of III dissolved in 130 ml of EtOH was irradiated under a condition identical with the photolysis of I until all of the starting material was consumed. Evaporation of the solvent followed by recrystallization of the residue afforded III′ in a quantitative yield.

Catalytic Reduction of Cyclohept[*b*]indol-10[5]-one (IVa)——Catalytic hydrogenation of IVa under the same condition as above resulted in the quantitative formation of the tetrahydro compound (XVa), mp 220—221° (MeOH), UV $\lambda_{max}^{95\%EtOH}$ nm (log ε): 213.5 (4.48), 245 (4.19), 268 (4.07) and 302 (4.09). This compound

Table XI. Melting points and Elemental Analysis of the Photo-products

Product	Molecular composition	Analysis (%) Calculated C	H	N	Found C	H	N	mp (°C)
IIa	$C_{13}H_9ON$	79.98	4.65	7.17	79.88	4.69	7.37	113—114
IIIa	$C_{13}H_9ON$	79.98	4.65	7.17	79.85	4.64	7.45	83—85
IVa	$C_{13}H_9ON$	79.98	4.65	7.17	79.79	4.67	7.31	285—286
Va	$C_{13}H_9ON$	79.98	4.65	7.17	79.91	4.63	7.20	250—252
VIa	$C_{13}H_9ON$	79.98	4.65	7.17	79.95	4.68	7.14	109—110
VIIIa (R=CH_3)	$C_{14}H_{13}O_2N$	73.99	5.77	6.16	74.01	5.80	5.95	105—106
VIIIa (R=Et)	$C_{15}H_{15}O_2N$	74.66	6.27	5.81	74.50	6.23	6.06	139—140
IIb	$C_{15}H_{13}ON$	80.69	5.87	6.27	80.98	5.67	6.38	137—139
IIIb	$C_{15}H_{13}ON$	80.69	5.87	6.27	80.63	5.65	6.21	157—159
III'b	$C_{15}H_{13}ON$	80.69	5.87	6.27	80.33	5.85	6.36	161—162
IVb	$C_{15}H_{13}ON$	80.69	5.87	6.27	81.01	5.79	6.33	>290
Vb	$C_{15}H_{13}ON$	80.69	5.87	6.27	80.58	5.89	6.13	232—235
VIb	$C_{15}H_{13}ON$	80.69	5.87	6.27	80.12	5.79	6.24	125—126
VIIIb (R=CH_3)	$C_{16}H_{17}O_2N$	75.27	6.71	5.49	75.56	6.68	5.39	138—140
VIc	$C_{14}H_{11}ON$	80.36	5.30	6.69	80.63	5.12	6.71	116—117
III'c	$C_{14}H_{11}ON$	80.36	5.30	6.69	80.36	5.30	6.69	136—139
VIIc	$C_{14}H_{11}ON$	80.36	5.30	6.69	79.90	4.98	6.80	88—90
VII'c	$C_{14}H_{11}ON$	80.36	5.30	6.69	80.25	5.21	6.75	82—85
IId	$C_{16}H_{15}ON$	80.98	6.37	5.90	80.78	6.35	5.85	188—189
IIId	$C_{16}H_{15}ON$	80.98	6.37	5.90	80.55	6.36	6.00	90—92
III'd	$C_{16}H_{15}ON$	80.98	6.37	5.90	80.87	6.25	5.91	164—167
VId	$C_{16}H_{15}ON$	80.98	6.37	5.90	80.88	6.38	5.93	134—136
VII'd	$C_{16}H_{15}ON$	80.98	6.37	5.90	81.11	6.40	5.83	51—52
IIe	$C_{17}H_{17}ON$	81.24	6.82	5.57	81.08	6.79	5.67	127—128
IIIe	$C_{17}H_{17}ON$	81.24	6.82	5.57	81.16	6.85	5.76	111—113
III'e	$C_{17}H_{17}ON$	81.24	6.82	5.57	81.24	6.82	5.57	112—113
VIe	$C_{17}H_{17}ON$	81.24	6.82	5.57	81.21	6.78	5.68	138—140
IIf	$C_{14}H_8ON_2$	76.36	3.66	12.72	76.64	3.47	12.96	132—135
IIIf	$C_{14}H_8ON_2$	76.36	3.66	12.72	76.65	3.67	12.99	137—138
III'f	$C_{14}H_8ON_2$	76.36	3.66	12.72	76.54	3.61	12.63	176—177
VIf	$C_{14}H_8ON_2$	76.36	3.66	12.72	75.91	3.74	12.43	201—204
IIg	$C_{16}H_{12}ON_2$	77.40	4.87	11.28	76.76	4.87	10.85	173—174
IIIg	$C_{16}H_{12}ON_2$	77.40	4.87	11.28	77.15	4.79	11.08	161—162
III'g	$C_{16}H_{12}ON_2$	77.40	4.87	11.28	76.98	4.78	11.13	179—180
VIg	$C_{16}H_{12}ON_2$	77.40	4.87	11.28	77.08	4.91	11.39	210—212

was identified with 10-oxo-5,6,7,8,9,10-hexahydrocyclohept[*b*]indole obtained by the photolysis of tetrahydroacridine 10-oxide.[24]

Catalytic Hydrogenation of IVb——Two hundred milligrams of IVb was hydrogenated in 50 ml of acetic acid in presence of 10% Pd/C (50 mg). The hydrogen absorption was observed only if the solution was warmed at *ca.* 40°. Evaporation of the filtrate followed by recrystallization of the residue from MeOH afforded the pure tetrahydro compound (XVb), mp 287—288°. Its UV spectrum is quite similar to that of XVa. *Anal.* Calcd. for $C_{15}H_{17}ON$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.15; H, 7.59; N, 6.26. Non-identity of this material with Xb (mp 290—295°) obtained from IIb was assured by the depression of the mixed melting point.

Catalytic Hydrogenation of Vb——The compound (Vb) was hydrogenated under the same conditions as described above. The tetrahydro compound (XVIb) (185 mg) was obtained, mp 168—169°. IR ν_{max}^{KBr} cm^{-1}: 3260, 1620, 820. UV $\lambda_{max}^{95\%EtOH}$ nm (log ε): 240 (4.21), 316 (4.35). Its NMR spectrum is reported in ref. 2*c*.

Catalytic Hydrogenation of 5-Methyl-10-oxo-10H-azepino[1,2-*a*]indole (VIc)——Catalytic hydrogenation of VIc in EtOH over 5% Pd/C at room temperature afforded the corresponding tetrahydro compond (XVIIc), mp 54—55°, in 75% yield; *m/e*: 213 (M^+). Its structure was determined to be 5-methyl-10-oxo-6,7,8,9-tetrahydroazepino[1,2-*a*]indole by a mixed melting point determination with the authentic sample.[24]

Under the identical condition, VIg was hydrogenated to XVIIg, mp 88—91° (hexane) in a high yield, *m/e*: 252 (M^+).

Synthesis of Methyl Derivatives of Dibenz[*b*,*f*][1,4]oxazepines (VII'c and VII'd)——This synthesis was achieved by the following three steps; i) *o*-Bromonitrobenzene (or 3-bromo-4-nitrotoluene) (3 g) was mixed with the potassium salt of phenol (or *p*-cresol) (3 g). After adding 1 g of Cu powder (activated by washing with acetone containing 1% of I_2), the whole mixture was heated at 150—160° under stirring for 30 min, poured into ice-water, and the whole was extracted with ether. Ether layer was then dried and evaporated. The residue obtained was chromatographed over Al_2O_3. The corresponding diphenyl ether was obtained in a satisfactory yield (*ca.* 2.5—3.3 g). *o*-Nitrodiphenyl ether, mp 47—49°, and 2-nitro-5,4'-dimethyldiphenyl ether, mp 87—88°. ii) One gram of the diphenyl ether was hydrogenated over Raney Ni (T-1) in 100 ml of EtOH at room temperature. After filtration, the solvent was evaporated under a reduced pressure. The crude hydrogenated product was then acetylated by warming with Ac_2O–AcOH (1: 1, v/v) for 20 min. The usual work-up afforded the corresponding *o*-acetoaminodiphenyl ether (mp 83—85° for the unsubstituted one and an oil for the dimethyl derivative) again in a good yield (800—900 mg). iii) The diphenyl ether (1 g) was heated in polyphosphoric acid (8 g) at 150—160° under stirring for 3 hr. When cooled, the whole was poured into H_2O and extracted with ether. The ether layer, after washing with 5% K_2CO_3 and dried over $MgSO_4$, was evaporated. Recrystallization of the residue from ether–hexane gave VII' (VII'c and VII'd) in 40—50% yield. The synthesized compounds were identified with the photoproducts obtained as above.

Reactions of VIIIa——The solution of VIIIa (100 mg) dissolved in 100 ml of EtOH, added with 3 drops of conc. HCl, was kept standing at room temperature for 3 hr and then evaporated under a reduced pressure (at room temperature). By chromatography over Al_2O_3, 90 mg of diphenylamine derivative (XIXa) was obtained, mp 121—122°. *Anal.* Calcd. for $C_{13}H_{11}O_2N$: C, 73.22; H, 5.20; N, 6.57. Found: C, 74.02; H, 5.58; N, 6.43.

A solution of XIXa (350 mg) dissolved in 100 ml of EtOH, after addition of 10 drops of conc. HCl, was refluxed for 4 hr. Evaporation of the solvent followed by recrystallization of the residue from MeOH afforded 300 mg of the HCl salt of 4-hydroxyacridine (XXa). By neutralization with $NaHCO_3$ solution, the free base was obtained, mp 122—123° (HCl salt, mp 242°). *Anal.* Calcd. for $C_{13}H_9ON$: C, 79.98; H, 4.65; N, 7.17. Found: C, 80.12; H, 4.75; N, 7.01.

If VIIIa was used instead of XIXa, XXa was obtained in *ca.* 60% yield.

Conversion of VIIIb to 1,7-Dimethylacridin-4-ol (XXb)——By the same condition as above, VIIIb was converted to XXb in 80—85% yield, mp 132—133.5° (HCl salt: red crystals, mp 265°). *Anal.* Calcd. for $C_{15}H_{13}ON$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.76; H, 5.92; N, 6.38.

Reduction of VIIIa with $LiAlH_4$——Two hundred milligrams of VIIIa was reduced with 100 mg of $LiAlH_4$ in ether at room temperature. After 3 hr, excess of the reagent was decomposed with wet Na_2SO_4 and the product was taken into ether. Evaporation of ether after drying afforded 2-methoxymethyl-2'-hydroxydiphenylamine in 85% yield, mp 101—102°. *Anal.* Calcd. for $C_{14}H_{15}O_2N$: C, 73.34; H, 6.59; N; 6.11. Found: C, 73.15; H, 6.70; N, 6.05.