IDENTIFICATION OF THE PRESENCE OF UNSTABLE INTERMEDIATE

IN THE PHOTOLYSES OF ACRIDINE 10-OXIDES[1]

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In the preceding paper,[3] we reported results of the photolysis of 2,7-dimethyl-
acridine 10-oxide (1b).* These and previous investigations[4-6] in the photolyses
of acridine 10-oxides pointed to the formation of the 1,2-oxazepine intermediate
(B) from the initially formed oxaziridine species (A).

This paper reports trapping of the 1,2-oxazepine (B) by methoxide ion and the
other reactions of this intermediate.

A 0.2% solution of acridine 10-oxide (1a) in dry benzene was irradiated.**
The reaction was monitored by periodical measurements of the uv spectrum (above
340 nm region) in a diluted benzene solution. As soon as all of the N-oxide was
consumed, the irradiation was terminated and the solution was then subjected
rapidly to the following reactions in the dark; (i) stirred for several hr after
addition of one-fifth volume of methanol containing 5% of triethylamine, (ii)
flashed with HCl gas for a few min, and (iii) refluxed for several hr or kept
standing for 24 hr at room temperature. These results were compared with that
obtained by the longer irradiation experiment (iv)*** in which the irradiation
was continued two or three times longer than that necessary to obtain the above
shortly irradiated solution. The related N-oxides (1b and 1c) gave similar
results. Table I summarized these results.

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*   For convenience, the same numerals (1-8) and alphabet (A-G) with the preced-
    ing paper are used for representing the compounds and intermediates.
** Photolyses were carried out in an immersion apparatus with Pyrex filter and
    450 W high-pressure mercury arc lamp.
*** The results reported in our previous papers[3-6] corresponded to this longer
    irradiation experiment. Reproducable product distributions were obtained
    irrespective to the work-up method under these conditions.

Table I. Yields and Mp of Products[a-c]

N-oxide	reaction condition	recovered[d] N-oxide 1	I 2	I 3[e]	5	II 6	7	III 8
	mp	169-171°	113-114°	83-85°	109-110°	285-286°	250-252°	111-115°
1a	i	5%	~	-	2%	10%	10%	60%
	ii	3%	-	-	2%	60%	10%	-
	iv	-	-	-	5%	30%	20%	-
	mp	183-185°	137-139°	157-159°	125-126°	>290°	232-235°	138-140°
1b	i	14%	19%	39%	2%	-	18%	-
	ii	16%	-	-	3%	48%	14%	-
	iii	16%	16%	35%	2%	-	18%	-
	iv	-	8%	13%	4%	13%	40%	-
	mp	177°(dec)			116-117°			13(89-90°)
1c	i	68%			8%			5%
	iii	68%			8%			5%
	iv	13%			12%			10%

a) Yields are based on the starting N-oxides.
b) All structures were supported with analytical and spectroscopic evidence.
c) 2a and 3a were obtained by the irradiation of 1a in aq. CH_3CN, and 8b was obtained from 1b in methanol. Details will be reported in full paper.
d) The N-oxides were synthesized from the parent amines by oxidation with perbenzoic acid. If impure N-oxides were used in these photolyses, the yields of 6 increased appreciably.
e) The combined yield of 3 and 4. It was found in the separate experiments that 3 cyclized to 4 by irradiation.

From the results shown in the Table, it is obvious that an unstable intermediate exists in the shortly irradiated solution of the respective N-oxides and is undergoing a variety of thermal and photochemical reactions. Though the actual isolation of the intermediate has not been achived as yet,* its structure can be deduced as the oxazepine (B) from the following data; (1) the solvent addition product (8a) was obtained as a major product from 1a under the experiment-i[7] and (2) the product (13c)** was obtained from 1c in the experiments i∼iv.

The formation of an unstable intermediate from 1c was further supported by uv spectrometry. Thus, if 10^{-4} M solution of 1c in dry benzene was photolyzed externally by >300 nm ray, the original longest wavelength maxima at 442 and

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* The stability of the intermediates decreased dramatically upon concentration.
** The compound (13c) rearranged to 11-methyldibenz[b,f]-1,4-oxazepine, mp 82-84°, in the course of silicagel column chromatography. The structure of the latter was confirmed by the synthesis reported in reference 8.

467 nm of the N-oxide shifted to 407 nm within a few min. By short warming of
this solution at 60°, this maximum again shifted back to those of the N-oxide.
Such a trend of the intermediate was also indicated by the high yield recovery
of the N-oxide (Ic) in the experiments-i and -iii.

The final confirmation of the structure of the intermediate was provided by
LiAlH$_4$ reduction of the shortly irradiated solution of 1a affording an oily
hydroxyamino compound (15a) in 30-35% yield. Its structure was supported by uv
spectra indicating the presence of aniline and phenol functions in the molecule
(in EtOH; two maxima at 276 and 282 nm, in diluted HCl; at 278, and in aq. KOH;
at 295 nm). The spectra of its crystalline diacetate (16a), mp 118-120°, further
confirmed the proposed formulation [ir (KBr); 3280, 1750, and 1655 cm^{-1} and nmr
(CDCl$_3$); 8.10 (3H,s), 7.70 (3H,s), 6.22 (2H,s) and 2.1-3.2τ(8H,m)].

The reactions of the 1,2-oxazepine intermediates are summarized in Scheme 1.
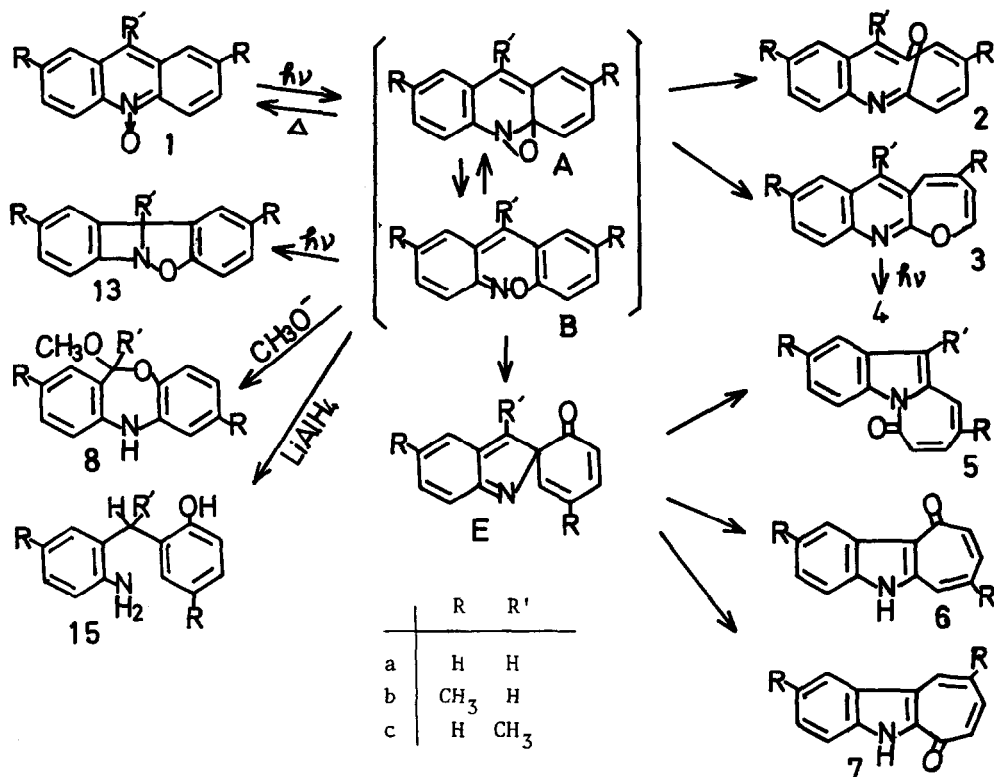
Scheme 1

It is surprizing that except the obviously photochemical pathways (designated by hν), almost all of the pathways (designated by a simple arrow) shown in the Scheme can proceed under thermal conditions. We may, therefore, conclude that while some of these pathways can also proceed photochemically (for example, a pathway from B to E might proceed by photochemical 1,3-suprafacial nitrogen shift) all of the essential pathways after the oxaziridine formation can be explained by the thermal reactions of the two equilibrated intermediates (A and B). The presence of the unstable intermediates as demonstrated by the present investigation not only supports the previously proposed mechanism[3-6] but also seems to open a new area in the photolyses of the related aromatic amine oxides.[9]

<div align="center">REFERENCES</div>

1) This paper forms Part XX of "Studies on the N-Oxides of π-Deficient N-Hetero-aromatics", and also Part X of "Photochemistry of Heterocyclic Compounds". Preceding paper, see reference 3.

2) Address correspondence to this author.

3) Sa. Yamada, M. Ishikawa, and C. Kaneko, preceding communication.

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

5) C. Kaneko, Sa. Yamada, and M. Ishikawa, Chem. Pharm. Bull.(Tokyo), 17, 1294 (1969).

6) C. Kaneko, Sa. Yamada, and M. Ishikawa, Tetrahedron Letters, 1970, 2329.

7) Under a comparable condition, SEt ion also reacted with the intermediate to give the corresponding addition product.

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

9) The products via an 1,2-oxazepine intermediate were obtained from the N-oxide whose oxaziridine is expected to have less (or at least the same) thermal stability than (or to) the corresponding 1,2-oxazepine. Pyridine 1-oxides and their aza-derivatives fall in this category. Thus, essentially the same phenomenon can be expected in these photolyses. For detailed discussion, see, M. Ishikawa, C. Kaneko, I. Yokoe, and Sa. Yamada, Tetrahedron, 25, 295 (1969).

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