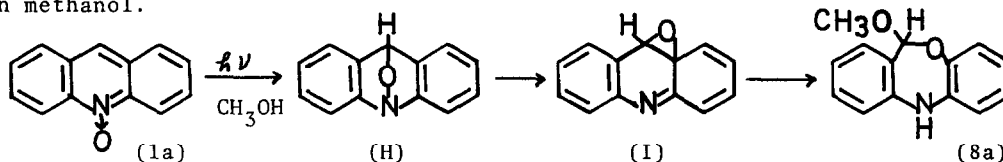PHOTOLYSIS OF 2,7-DIMETHYLACRIDINE 10-OXIDE[1]

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Previously, we have reported the photochemical isomerization reactions of
acridine 10-oxide (1a),[2] its substituted derivatives,[3] and benz[a]acridine 7-
oxides[4] and proposed the mechanisms in which the corresponding oxaziridines
(e.g., A) were assumed as the key intermediates. A different mechanism including
9,10-epoxyacridine (H) was proposed by Mantsch[5] in order to account for the for-
mation of the solvent addition product (8a) obtained from 1a by the irradiation
in methanol.

To solve the obvious discrepancy between these two mechanisms and also to
clarify such a large solvent effect in these photolyses, we have irradiated 2,7-
dimethylacridine 10-oxide (1b) in methanol or benzene as a typical hydroxylic or
non-hydroxylic solvent. The results are summarized in Table I.

Table I. Yields and Mp of Photo-products[a]

Product Solvent	I			II			III
	2b 137-139°	3b 157-159°	4b 161-162°	5b 125-126°	6b >290°	7b 232-235°	8b 138-140°
CH₃OH	20%	5%	45%	±	2%	±	7%
benzene	8%	12%	±	4%	13%	40%	-

a) Photolyses were carried out in an immersion apparatus with Pyrex filter and a
450 W high-pressure marcury arc lamp.

The spectral properties of these products and some of their derivatives are pre-
sented in Table II. The structures of 2b~5b were unequivocally determined from

the comparisons of the nmr spectra with those of the closely related compounds obtained in our previous experiments.[2-4] Though the comparison of the spectral data between 8b and 8a indicated their close relationship, the position of one of the methyl groups in 8b was not the same with the one as expected from the mechanism proposed by Mantsch.[5] This conclusion was based on the nmr spectrum of the acridin-4-ol (9b), mp 132-133°, obtained from 8b by refluxing in methanol containing conc. HCl. The presence of two vicinal protons on the phenol ring was clearly demonstrated by the large coupling constant (7 Hz).

Table II.   Uv and Nmr Spectra of New Compounds[*]

Comp.	uv(EtOH) nm(log ε)		nmr(a:CDCl$_3$, b:CF$_3$COOH): τ (Hz) solv. methyl and ring protons			
2b	270(4.65)	358(3.66)	a	7.62s(3H) 7.50s(3H)	3.00d(11,1H) 2.45d(8,1H)	2.70s(2H) 2.30s(1H)	2.70d(11,1H) 2.08d(8,1H)
3b	213(4.70) 320(4.08)	225(4.29)	a	8.00s(3H) 7.50s(3H)	4.58d(6,1H) 2.56d(8,1H) 2.22d(8,1H)	3.60s(1H) 2.53s(1H)	3.58d(6,1H) 2.32d(8,1H)
4b	215(4.76) 249(4.38) 324(3.93)	245(4.39) 278(3.87) 339(3.97)	a	8.15s(3H) 7.50s(3H)	5.70m(1H) 2.60d(8,1H) 2.20s(1H)	4.55m(1H) 2.53s(1H)	4.10m(1H) 2.25d(8,1H)
5b	258(4.29) 430(3.45)	291(4.54)	a	7.80s(3H) 7.50s(3H)	3.58d(13,1H) 2.94s(1H) 1.13d(8,1H)	3.28d(13,1H) 2.71d(8,1H)	3.16s(1H) 2.52s(1H)
6b	221(4.57) 302(4.39)	241(4.44) 382(3.98)	b	7.30s(3H) 7.08s(3H)	2.22s(2H) 1.50s(1H)	2.00d(13,1H) 1.37s(1H)	1.83d(13,1H)
7b	230(4.43) 280(4.31) 410(3.89)	273(4.30) 327(4.27)	b	7.33s(3H) 7.00s(3H)	2.20s(2H) 1.65d(12,1H)	1.88d(12,1H) 0.73s(1H)	1.73s(1H)
8b	292(4.40)		a	7.75s(6H) 6.38s(3H)	4.25s(1H) 3.03d(8,1H)	3.43s(1H) 2.98d(8,1H)	3.37d(8,2H) 2.83s(1H)
9b	243(4.45) 346(3.43) 364(3.61)	265(4.76) 356(3.41) 403(3.52)	a	7.46s(3H) 7.37s(3H)	2.93d(7,1H) 2.20s(1H)	2.75d(7,1H) 1.87d(9,1H)	2.35d(9,1H) 1.27s(1H)
10	218(4.55) 272(4.18)	249(4.34) 303(4.19)	b	8.76d(7,3H) 7.45s(3H)	6.4-7.1m(4H) 1.95s(1H)	7.5-8.3m(3H)	2.60s(2H)
11	240(4.21)	316(4.35)	a	8.83d(7,3H) 7.53s(3H)	6.6-7.4m(4H) 2.67d(9,1H)	7.8-8.4m(3H) 2.53s(1H)	2.80d(9,1H) 1.00s(1H)
12	218(4.50) 272(4.15)	249(4.30) 303(4.15)	b	8.75d(7,3H) 7.50s(3H)	6.4-7.1m(4H) 1.98s(1H)	7.5-8.3m(3H)	2.63s(2H)

[*] All compounds showed satisfactory elemental analyses and the structures were also supported by ir and mass spectra.
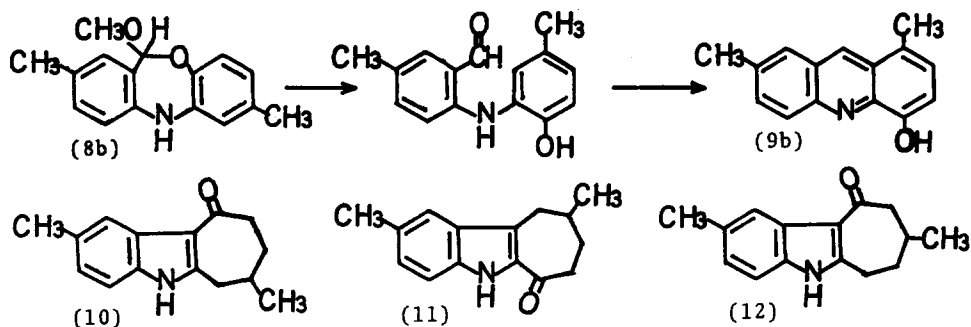
The photo-products (6b and 7b) were reduced by catalytic hydrogenation with Pd/C to the tetrahydro compounds (10, mp 287-288° and 11, mp 168-169°), whose uv spectra resembled closely to those of 3- and 2-acylindoles. In our previous experiments,[2-4] it was found that the same reduction of a 2-type annulene gave such acylindole, whose formation could be reasonably explained as proceeded via the valence bond tautomer (C). As expected, the reduction of 2b afforded the tetrahydro compound [12, mp 290-295(decomp)] and 2,7-dimethylacridine in the respective yields of 36 and 12%. Though the former product (12) exhibited almost the same spectral properties with 10, the mixed mp determination revealed their non-identity. The structure of 6b, therefore, was deduced as the most plausible one. The position of the methyl group of the other photo-product (7b) was provided from the inspection of the ring proton region of its nmr spectrum. The fine splitting of the high-field doublets and the appearance of a singlet at a lower field due to the protons on the seven-membered ring indicated the presence of 4-methyl-2,4-dienone function.

From the solvent effects upon the product-formations and on the basis of the structure of each product, the products could be reasonably divided into three groups (I-III as shown in Table I). According to this classification, the following might be concluded in the present photolyses; i) the formation of I-products was prefered in methanol, while that of II-products predominated in benzene, ii) III-product was formed only in methanol, and iii) the methyl position in II- and III-products could be reasonably explained only if we considered the participation of the spiro-intermediates (e.g., E and G).
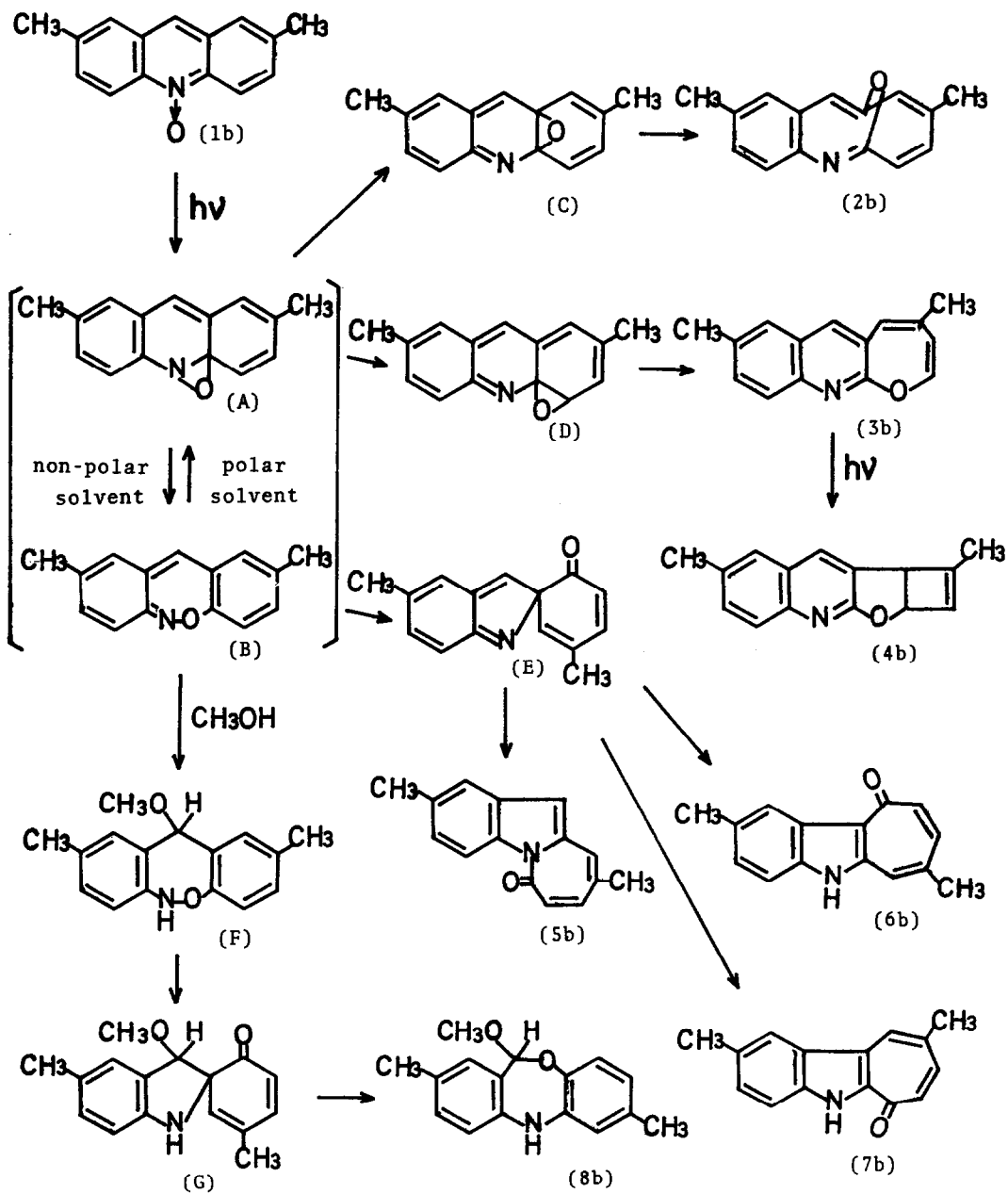
Scheme 1.

The mechanism accounting for all of them is shown in Scheme 1.

The oxaziridine (A)[6,7] formed from the photo-excited N-oxide (1b) equilibrates with its valence bond tautomer, the 1,2-oxazepine (B). The former species exists preferentially in a polar medium, while the latter species predominates over the other species in a non-polar 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.[8] The former species (A) affords I-products by 1,5- or 1,9-oxygen shift. The latter species (B) rearranges to the spiro-compound (E) which in turn affords II-products by the subsequent C-C bond fission and recyclization. An almost exclusive formation of 8a from 1a by irradiation in methanol[5] necessarily suggests that the addition of methanol should occur at the equilibration stage (A⇌B) to B-species, because otherwise (e.g., addition of methanol to E-species, etc.) the high polarity of the solvent should have increased the yields of I-products.

The more detailed study of the photolyses of acridine 10-oxide derivatives also supported the present mechanism and the subsequent paper reports the successful identification of the presumed intermediates as well as the nature of the reaction pathways (thermal or photochemical) indicated in Scheme 1.

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