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IRRADIATION OF N-OXIDES OF α-CYANOAZANAPHTHALENES IN AN APROTIC SOLVENT.

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We have recently reported on the irradiation of quinoline 1-oxides,[2-4] isoquinoline 2-oxides,[2,3] and phenanthridine 5-oxides[3] in protic solvents by a high-pressure mercury lamp. In view of the current interest in such irradiation reactions,[5a-f] we wish to report the extension of this study to include photochemical reaction of α-cyanoazanaphthalene N-oxides by the same light source in an aprotic solvent.

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1) A part of this study will be published in detail as Part II of a series entitled "Three-membered Ring System with Two Hetero Atoms" in the Rept. Res. Inst. Dental Materials, Tokyo Medico-Dental University, 8 (1966).

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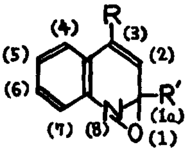
4) C. Kaneko and S. Yamada, ibid., 14 (1966), in press.

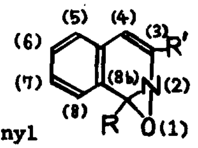
5) (a) O. Buchardt, Acta Chem. Scand., 17, 1461 (1963). (b) O. Buchardt, J. Becher, and Chr. Lohse, ibid., 19, 1120 (1965). (c) G. B. Brown, G. Levin, and S. Murphy, Biochem., 3, 880 (1964). (d) F. Cramer, and G. Schlingloff, Tetrahedron Letters, 1964, 3201. (e) E. C. Taylor, B. Furth, and M. Pfau, J. Amer. Chem. Soc., 87, 1400 (1965). (f) O. L. Chapmann, Advan. Photochem., 1, 410 (1963).

Irradiation of 2-cyano-4-chloroquinoline 1-oxide in dichloromethane solution under nitrogen atmosphere, using 100-w. Hanovia immersion lamp and a Pyrex filter, resulted in the formation of (Id), m.p. 94-95° (from hexane), in 80% yield. Elemental analysis and molecular weight determination established the empirical formula of (Id) as $C_{10}H_5ON_2Cl$. The n.m.r. spectrum[6] of (Id) in $CDCl_3$ showed the absorptions at 2.70-2.82 τ (4H, multiplet) and at 3.53 τ (1H, singlet). As shown in Table 1, the ultraviolet absorption spectrum of



(I)

Ia: R = CH_3, R' = CN
Ib: R = H, R' = CN
Ic: R = H, R' = phenyl
Id: R = Cl, R' = CN



(II)

IIa: R = CN
R' = H
IIb: R = CN
R' = CH_3

TABLE 1.

Ultraviolet Absorption Spectra of Oxaziranes in 95% EtOH.

Compound	mμ	log ε	mμ	log ε
(Ia)[4]	239.0	4.42	315.0	3.50
(Ib)[4]	240.0	4.51	322.0	3.56
(Ic)[4]	251.0	4.50	317.0	3.83
(Id)	242.0	4.40	325.0	3.58
(IIa)*	245.5 253.0	3.90 3.86	345.0	3.68
(IIb)*	248.0 255.0	3.97 3.93	350.0	3.61

* The spectra of (IIa) and (IIb) change slowly on standing at room temperature in a dark room.

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6) N.m.r. data were obtained on a JNM-3H-60 spectrometer operated at 60 Mc. The chemical shifts are given in τ-unit.

(Id) is very similar to those of (Ia) to (Ic), whose syntheses and identifications have been described previously.[4]

Structure (Id) is the only structure consistent with these data. On the contrary, irradiation of 2-cyano-4-methoxyquinoline 1-oxide under the same conditions gave rise to somewhat unexpected product (III), m.p. 205-208°, whose analytical values agreed with $C_{11}H_8O_2N_2$ (isomeric to both the corresponding oxazirane and starting 1-oxide) after solvent evaporation and purification by recrystallisation from acetone in 80% yield. Its phenolic nature is sufficient to eliminate the corresponding oxazirane structure (Ie) for this compound. The n.m.r. spectrum of (III) in dimethylsulfoxide showed the absorptions at 1.8-2.4 τ (4H, multiplet due to aromatic protons) and at 5.95 τ (3H, due to protons on MeO-group). The ultraviolet absorption spectra of (III) is quite similar to those of 3-hydroxy-2-cyanolepidine (IV) (*vide infra*) as shown in Table 2.

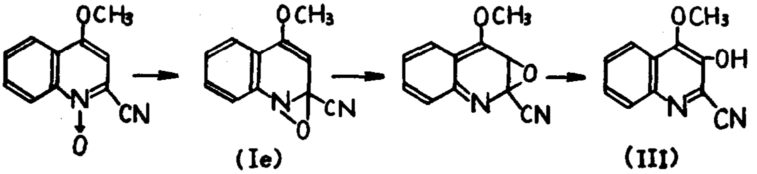
TABLE 2.

Ultraviolet Absorption Spectra of (III) and (IV).

Compound	Solvent	mμ	log ε	mμ	log ε	mμ	log ε	mμ	log ε
(III)	95% EtOH	239.5	4.89	303.0 293.5	3.92 3.96	360	3.68	420	3.39
	5% K_2CO_3	247.5	4.65	302.0 312.0	3.40 3.35	409	3.75		
(IV)	95% EtOH	236.0	4.79	294.5 304.0	3.95 3.90	358	3.55	420	3.41
	5% K_2CO_3	246.5	4.73	303.0 314.0	3.68 3.68	410	3.85		

Considering these data, structure (III) can now be given to this phenolic compound. We consider that this conversion proceeds by initial formation and subsequent rearrangement of the oxazirane (Ie).

We have observed that (Ia) is converted to (IV), m.p. >320°., $C_{11}H_8ON_2$, on dissolving the former in trifluoroacetic acid. Structure of 3-hydroxy-2-cyanolepidine was assigned to (IV) from spectroscopic data (UV, IR and n.m.r.) and confirmed by hydrolysis and decarboxylation to 3-hydroxylepidine, m.p. 198-199°, identical with an authentic sample.[7] Addition of bromine to (Ia) in dichloromethane solution also resulted in the formation of (IV) in completely anhydrous condition. Considering these observations, together with the fact that both reactions proceed almost quantitatively in a dark room, it may be concluded that the rearrangement of (Ie) to (III) proceeds intramolecularly, and is not photochemical in nature. These considerations led us to propose the following pathway for this novel rearrangement.[8]



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[7] G. Kobayashi, S. Furukawa, Y. Akimoto, and T. Hoshi, Yakugaku Zasshi, 74, 791 (1954).

[8] We have found that most of (I)-type oxaziranes can be transformed to the corresponding 3-hydroxy compounds under quite mild conditions in a dark room. Details of this interesting transformation will be reported soon.

Though the oxaziranes (Ia-Ic) are very stable in solid state or in aprotic solvents, it is found from experiments so far made on these oxaziranes since their isolation[4] that they are rather unstable in a protic solvent.

This and the fact that most of the stable oxaziranes of (I)-type have a cyano group on the carbon atom (C_{1a} in I) common to both pyridine and epoxy rings, irradiation of 1-cyanoisoquinoline 2-oxide in dichloromethane was carried out in order to obtain the corresponding oxazirane having so far unknown 8b*H*-oxazirino[2,3-*a*]isoquinoline system (II). Actually, irradiation of (II) resulted in the formation of (IIa), m.p. 100-102° (from hexane), $C_{10}H_6ON_2$. Elemental analysis and molecular weight determination of (IIa) support the correctness of the assigned structure. The n.m.r. spectrum of (IIa) in $CDCl_3$ shows the absorptions at 2.50-3.10 τ (4H, multiplet due to aromatic protons) and two sets of doublet centered at 3.32 τ and 3.48 τ (1H each, j=7.8 cps.), and the latter two sets of doublet clearly indicate the presence of 1,2-epoxy function and exclude the presence of 2,3-epoxy function in (IIa). Similary, (IIb), m.p. 87-88° (from hexane), $C_{11}H_8ON_2$, was obtained from 3-methyl-1-cyanoisoquinoline 2-oxide. Compared to the stability of (Ia)-(Id) to the irradiation of wavelength longer than 300 mμ, the high sensibility of (IIa) and (IIb) to this irradiation[9] is worthy of

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[9] Further irradiation of (IIa) and (IIb) in benzene caused their decomposition, while so far no definite compounds have been isolated.

note. Irradiation of these compounds should be stopped by the time that half of the 2-oxides are consumed in the irradiation mixture. In this condition, the yield of (IIa) and (IIb) is 30-40% of the 2-oxides consumed. One of the reasons for this photosensibility of (IIa) and (IIb) may be due to the fact that the longest absorption maxima of these two oxaziranes are in a far longer wavelength than those of (Ia) to (Id).

These observations give direct evidence to support the currently accepted mechanism[2,3,5a,c,e,f] that the products of photolyses of the N-oxides of azanaphthalene and their higher benzenoid homologs can, in part, be rationalized in terms of corresponding oxazirane intermediates.

Further syntheses of (I)- and (II)-type compounds and their reactions are now under examination.

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