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A PHOTOCHEMICAL 1,2-DEUTERIUM SHIFT. IRRADIATION OF QUINOLINE N-OXIDE AND QUINOLINE N-OXIDE-2-d_1. (1)

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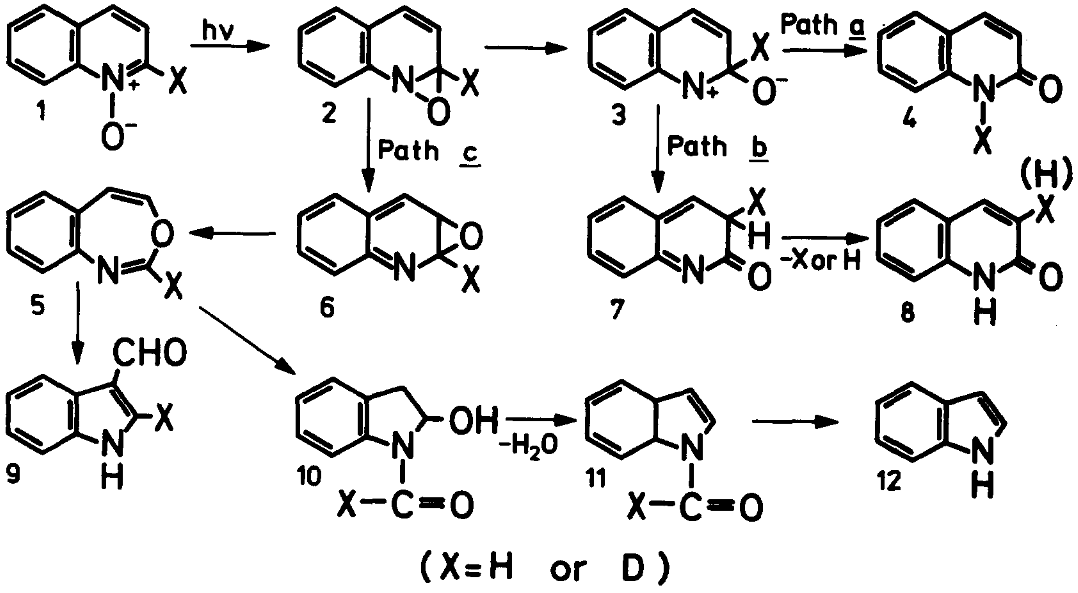
We have proposed a general mechanism for the light-induced isomerization of heteroaromatic N-oxides using the quinoline N-oxide system as a model (3). In order to obtain further information about this mechanism we have examined the photochemistry of quinoline N-oxide-2-d_1 and re-examined that of quinoline N-oxide in several solvents. The results obtained, listed in Table 1, satisfactorily confirm the postulated mechanism (Scheme I).

Scheme I



According to our proposed mechanism (3) there are two pathways leading to carbostyrils, (a) via a C,N 1,2-shift, and (b) via a C,C 1,2-snift. The formation of carbostyril-3-d corresponds to b, whereas the observed lack of formation of any carbostyril-1-d does not shed any light on path a, since under the circumstances N-D could quite easily exchange to give N-H.

The isotope ratio observed at the 3-position of the carbostyril produced is $\frac{D}{H}$ = 2.11 for water, 1.1 for 95% ethanol, 0.97 for absolute ethanol, 0.73 for benzene and 0.58 for ether (4). If it is assumed that the isotope effect for loss of hydrogen from 7 would lead to $\frac{D}{H}$ = 3.5 [which is probably a maximum (5)] the $\frac{D}{H}$ ratio in water indicates that at least 85% of the carbostyril is formed via b in water and ca. 63% in ethanol and that in aprotic solvents such as benzene or ether the proportion formed via b drops further to ca. 55% and 45% respectively. Even though the isotope ratio is expected to fall with solvent polarity (6), the $\frac{D}{H}$ ratio of less than 1 for aprotic solvents definitely indicates that the amount of carbostyril formed via path a increases as the polarity of the solvent is decreased.

The complete deuterium retention in the formyl groups of the N-formyl-2-indolinol and N-formylindole and the total loss of deuterium in the indole again is in excellent agreement with the proposed mechanism (7).

We have furthermore identified a new product, i.e., indole-3-carboxaldehyde, from the irradiation of quinoline N-oxide in ethanol. If quinoline N-oxide-2-d_1 was employed, indole-3-carboxaldehyde-2-d_1 with complete retention and no scrambling of the deuterium was obtained. This type of product presumably results from a thermal rearrangement of the benz[d][1,3]oxazepine since it has previously been shown that isolable benz[d][1,3]oxazepines rearrange in this manner upon thermolysis (8). We propose that the observed formation of indole--3-carboxaldehyde in absolute or 95% ethanol is due to the slow addition of ethanol to the benz[d][1,3]oxazepine which permits thermolysis to occur. In aprotic solvents the small amount of water present is presumably bound quite closely to the hygroscopic quinoline N-oxide leading to a high concentration of water in the vicinity of the intermediate resulting in N-formylindolinol formation.

Table 1. Irradiation of Quinoline and Quinoline N-Oxide-2-d_1.

	Starting Material		Products											
Solvent	Quinoline N-oxide-d-2	Quinoline N-oxide	Carbostyril-3-d		N-Formylindolinol		N-Formylindole		Indole-3-carboxaldehyde		Indole		Dimer	
			%D	% Yield[a]	%D	% Yield	%D	% Yield	%D	% Yield	%D	% Yield	%D	% Yield
Ether[c]	500 mg		35	10	100	4.6	100	4.2		0	0	40.5		0
Ether[c]	1 g	1 g		b	51	10.5	51	1.5		0	0	16		0
Abs.EtOH	500 mg		49	24		0	100	1	100	4	0	1.3	51	13.9
Abs. EtOH	1 g	1 g		b		0	51	1.3	51	3.2	0	6.5		b
95% EtOH	500 mg		51	37		0	100	2	100	1.6	0	1.3	51	9
H_2O[d]	1 g		69	11		0		0		0		0		0
Benzene[c]	500 mg		42	10	100	17	100	16		0	0	5		0

[a] Average or best ±3. Determined by isolation from silicagel TLC.

[b] Not measured.

[c] Small amount of water present.

[d] The aqueous solution was extracted with $CHCl_3$ and the products separated by TLC.

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4. These ratios are the average of at least three determinations.
5. see e.g. R. P. Bell and J. E. Crooks, Proc. Roy. Soc., A, 286 285 (1965).
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7. The position of the deuterium was determined by ^1H NMR.
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