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PHOTOCYCLIZATION OF BENZOFURANCARBOXANILIDES. PHOTOREARRANGEMENT OF THE BENZODIHYDROFURAN SYSTEM TO 3-*o*-HYDROXYPHENYLQUINOLONES[1)]

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cis-Dihydrobenzofuro[2,3-c]quinolone (**4a**) and *cis*-dihydrobenzofuro-[3,2-c]quinolone (**5**) undergo photorearrangement, characteristic to the benzodihydrofuran system, leading to 3-*o*-hydroxyphenylquinolone (**6**). A plausible mechanism involving a cyclopropyl dienone (**12**) was discussed.

We have demonstrated that oxidative photocyclization of anilides of some heterocyclic carboxylic acids is a simple method for synthesizing a variety of heteroaromatics containing quinolone rings.[1a,2)] Furthermore, under anaerobic conditions, the anilides of condensed five-membered heterocycles such as benzothiophene (**1b**)[3a)] and indole (**1c**)[3b)] undergo nonoxidative photocyclization to yield *trans*- and *cis*-isomers (**2b**,**c** and **4b**,**c**), respectively, even selectively based on the choice of solvent. During the course of our study on this line, we have observed that certain benzodihydrofuran derivatives undergo unexpected photorearrangement as reported in the present paper.

Irradiation[4)] of benzofuran-2-carboxy-N-methylanilide (**1a**) in acetonitrile afforded *trans*-dihydrobenzofuroquinolone (**2a**) as a sole product. On irradiation in a benzene solution, compound **2a** was again obtained accompanied by its oxidized product (**3**). In a protic solvent system such as benzene : ethanol (9 : 1), the *cis*-compound (**4a**) turned out to be a major product in good agreement with our proposed general mechanism.[3)] Interestingly, three new products (**5**,**6**, **7**) were concomitantly isolated in substantial amounts, and their structures were assigned[5)] as shown in Scheme I. Similar products were also obtained from the photolysis of **1a** in other protic media. These results are summarized in Table I.

Scheme I

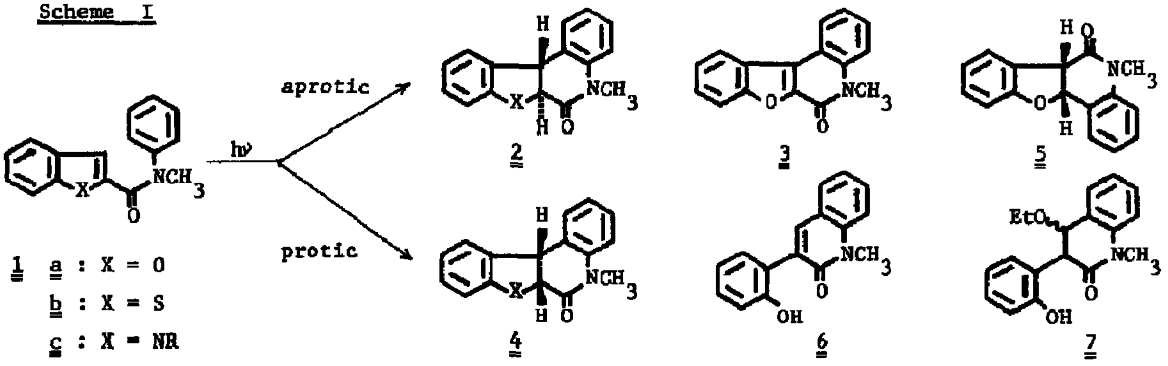

Table I Photoreactions of 1a (Irradiation time 2 hr)

Solvent	Yield (%) of						
	2a	3	4a	5	6	7	1a
	mp : 153-4°	182-3°	212-3.5°	145.5-7°	149.5-50°	171-3°	95-6.5°
acetonitrile	66	-	-	-	-	-	33
benzene	50	7	-	-	-	-	-
benzene:ethanol (9 : 1 v/v)	10	6	28	18	22	8	-
acetonitrile:water (9 : 1 v/v)	trace	12	12	9	51	-	-
ethanol	14	4	40	12	5	19	-

The origin of these products must be a result of photorearrangement since the quinolones (6,7) have a phenol moiety not at the 4- but at the 3-position, and the benzodihydrofuran (5) should be the product expected from, not 1a, but its positional isomer, the 3-carboxanilide (8). Therefore photocyclization of 8 was next examined (Table II and Scheme II). The reaction proceeded more slowly than that of 1a, and in benzene a normal trans-compound (9) was a sole product. In acetonitrile the reaction was more efficient and, in addition to 9, the quinolone (6) was isolated instead of the corresponding cis-isomer (5). In protic solvents, 6 was obtained in good yields. According to the general mechanism,[3)] the expected products are in aprotic solvent the trans-compound (9) by way of 10, and in protic solvent the cis-compound (5) by way of 11, respectively. In this photocyclization of 8, the absence of the cis-isomer (5) may suggest that the protonated intermediate (11) would preferably lead to 6 in place of 5, probably due to higher stability of 6 over 5.[6)]

The results of photolysis of 4a, as listed in Table III, confirm that in the photoreaction of 1a, compounds 5, 6 and 7 arise from the photorearrangement of initially formed 4a. Irradiation of 5 in ethanol gave also 6 and 7, but relatively slowly, indicating that the path (5→6)

Scheme II

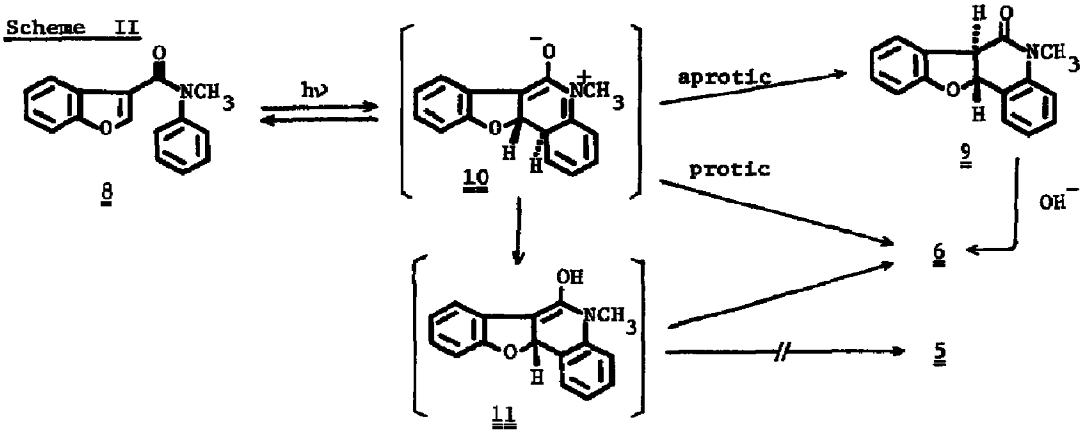

Table II Photoreactions of 8

Solvent	Time (hr)	Yield (%) of 6	 9 (mp 136.5-8°)	 8 (mp 94.5-6°)
acetonitrile	5	33	22	17
benzene	6	–	7	80
benzene:ethanol (9 : 1 v/v)	3	84	-	6
ethanol	3	84	-	15

Scheme III

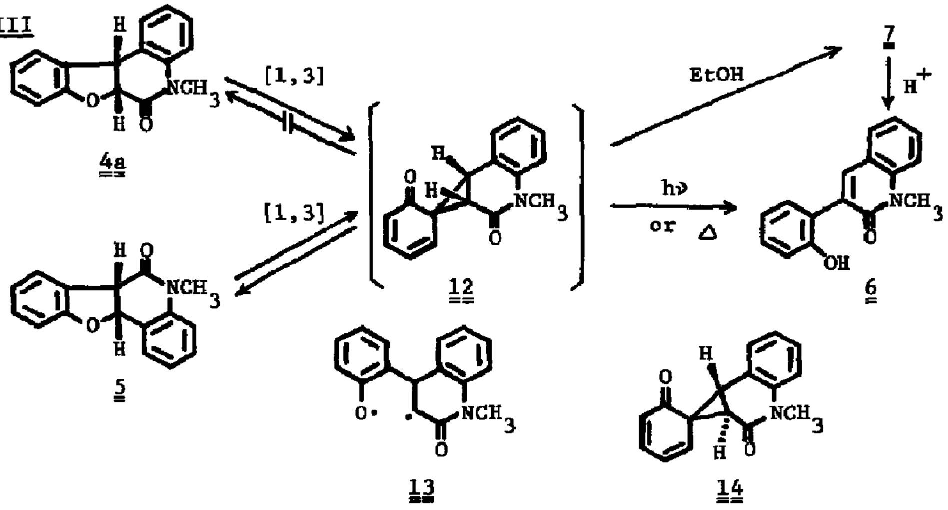

Table III Photoreactions of Dihydrobenzofuroquinolones (4a, 5)

Substrate	Solvent	Time (hr)	Yield (%) of 4a	 5	 6	 7
4a	acetonitrile	2.5	40	30	30	-
	ethanol	5	5	25	15	50
5	ethanol	5	–	60	5	20

is not a major one for the formation of **6** from **1a**. A reasonable mechanism is shown in Scheme III, which assumes the common intermediacy of a cyclopropyl dienone (**12**) from which all the rearranged products can be derived (photochemically and/or thermally).

Photochemical and thermal rearrangements involving the benzodihydrofuran and phenol system have some recent precedents. Schmid *et al.*,7) and Schultz *et al.*,8) both assumed the cyclopropyl dienone like **12** in such related systems, though two different mechanisms, homolytic7) and concerted,8) were postulated. It is noteworthy that, in contrast to the above photoreactivity of the *cis*-benzodihydrofuran (**4a**), the *trans*-counterpart (**2a**) is stable on irradiation. This remarkable dependency of the photoreactivity on the stereochemistry of the substrates is incompatible with the homolytic mechanism, because the homolytic carbon-oxygen cleavage in **4a** and **2a** should both produce the same biradical (**13**), which will readily lead to the key intermediate (**12**). Although the mechanistic details are still open to question, a concerted [1,3] sigmatropic rearrangement of **4a** and **5** to **12** is thus suggested in Scheme III. A similar rearrangement of **2a** must lead to the isomeric *trans*-dienone (**14**), which is unstable due to its highly strained ring structure, and is therefore improbable. This photorearrangement of the benzodihydrofuran system provides an interesting variation in the application of the photocyclization to syntheses of heterocycles.

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4) A solution of **1a** (200 mg, 0.8 mmoles) in a solvent (200 ml) was purged with nitrogen for 30 min. and then irradiated in a stream of nitrogen with a 100w high-pressure Hg lamp for 2 hr.

5) All new compounds gave satisfactory elemental analyses and showed reasonable spectral (uv, ir, ^{1}HNMR, and mass) properties.

6) Compound **5** was quantitatively converted into **6** on treatment with a base in few min. at room temperature.

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