

PHOTOREACTIONS OF AMIDES (XIII). PHOTOREARRANGEMENTS OF
THE BENZODIHYDROFURAN- AND BENZODIHYDROTHIOPHENE-CONTAINING HETEROCYCLIC SYSTEMS

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We have demonstrated that heterocyclic anilides undergo photocyclization in the absence of oxygen to afford the corresponding dihydroquinolone derivatives. During the course of our study on this line, we have observed that certain benzodihydrofuran 2a and benzo[b]dihydrothiophene 2b derivatives undergo unexpected photorearrangement.

Irradiation of benzofuran-2-carboxy-N-methylanilide 1a in a protic solvent system such as ethanol afforded *cis*-dihydrobenzofuro[2,3-*c*]quinolone 2a as a major product and three new products (3a, 4, 5). The origin of the latter must be a result of photorearrangement since the quinolones (3a, 4) 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-carboxyanilide 7a. The results of photolysis of 2a confirm that in the photoreaction of 1a, compound 3a, 4 and 5 arise from the photorearrangement of initially formed 2a.

In the case of benzo[b]thiophene-2-carboxy-N-methylanilide 1b, the similar photorearrangement occurred. Irradiation of 1b afforded benzo[b]thieno[3,2-*c*]quinolone 6 as a rearranged product. However, no photorearrangements were observed for dihydroindole derivatives 2c, the products from 1c.

Irradiation of anilides of these heterocyclic-3-carboxylic acids (7a, 7c) afforded compound 3a and 3c, respectively, which were formed by ring opening of the five-membered heterocycles. Mechanisms of these photoreactions were discussed.

