HETEROCYCLES, Vol. 9, No. 8, 1978

PHOTOCYCLIZATION OF HETEROCYCLIC ACYLANILIDES

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N- α,β-Unsaturated acylanilides, which contain various heterocyclic rings in their acyl groups, i.e., α-pyrone, α-furanone, α- and β-furans, and an ortho-substituent on the benzene ring, were found to undergo photocyclization to afford various products depending upon a heterocycle, and an ortho-substituent which brought about smooth photocyclization.

N- α,β-Unsaturated acylanilides have been known to undergo photocyclization under both oxidative and non-oxidative conditions.[1] Particularly, the photocyclization of the anilides having an ortho-electron withdrawing substituent proceeded smoothly and brought about suprafacial [1,5]sigmatropic shift of the substituent.[2] As an extension of the study on the photocyclization of these unsaturated systems, we now report the photocyclization of the N-heterocyclic acylanilides (1-4) which yielded various types of the condensed heterocycles depending upon the substituent present in the ortho-position (H, COOMe, and COOH).

The photochemical reactions described here were carried out in a benzene or benzene-methanol solution at room temperature with a low pressure mercury lamp.

Thus, irradiation of the δ-lactonic anilide (1,X=H) yielded the lactam (5)[3] under oxidative condition (I_2) and a mixture of lactams (6 and 7) under non-oxidative condition respectively. Spectral data of (6) [i.r.; ν 1710 (COOH), n.m.r.; δ 8.03 (1H, s, 4-H), 7.76 (1H, d, J=16Hz, R-C<u>H</u>=CH-COOH), 6.93 (1H, d, J=16Hz, R-CH=C<u>H</u>-COOH)] and the methyl ester of (7) [i.r.; ν 1710 (COOMe), mass.; m/e 468 (M^+), n.m.r.; δ 7.70 (2H, s, 2 × 4-H), 4.62 (4H, s, 4 × -CH)], confirmed their structures, thus suggested the formation process of (7) as being a dimeric photocycloaddition of the α,β-double bond of the acid (6)[4].

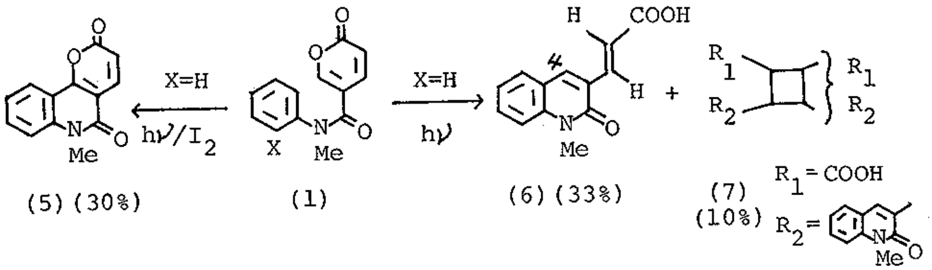
On the other hand, in the cases of the γ-lactonic anilides (2), the photocyclization was observed only when the anilide (2) was substituted with an ortho-carboxyl group. Though the unsubstituted γ-lactonic anilide (2,X=H) gave no photocyclized product irrespective of the condition employed, either oxidative or non-oxidative, the anilides carrying an ortho-electron withdrawing group (2,X=COOH) and (2,X=COOMe) underwent smooth photocyclization to afford the corresponding lactams (8,9, and 10) respectively.

The lactam (8), which was obtained from (2,X=COOH) by photocyclization at the root of the ortho substituent followed by spontaneous decarboxylation, showed the following spectral data [i.r.; ν 1780 (lactone), n.m.r.; δ 7.80-7.00 (4H, m, arom.H), 3.93 (1H, d, J=10Hz, 9b-H)].

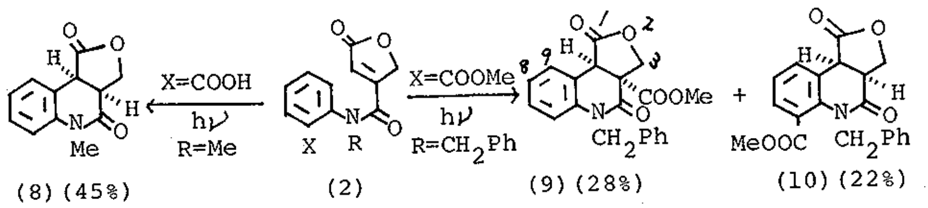
The lactam (9), formed from (2,X=COOMe) by photocyclization at the root of the ortho-ester group which simultaneously underwent [1,5]sigmatropic migration[2], exhibited the spectral data [i.r.; ν 1790 (lactone), 1740 (COOMe), n.m.r.; δ 7.70-7.00 (9H, m, arom.H), 4.30 (1H, s, 9b-H)], thus assured the structure.

The third lactam (10) was the product of photocyclization at the opposite site of the ester group and showed the spectral data [i.r.; ν 1780 (lactone), 1720 (COOMe), n.m.r.; δ 7.90-6.90 (8H, m, arom.H), 3.93 (1H, d, J=10Hz, 9b-H)].

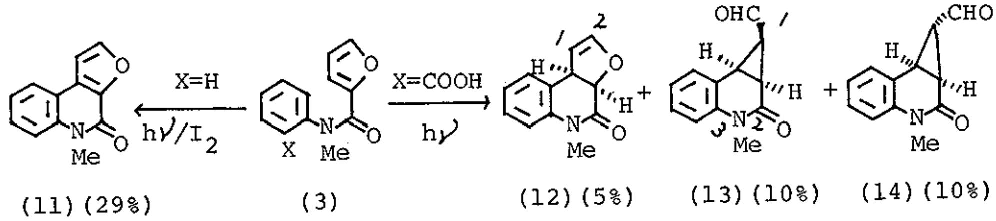
As the next examples of the photocyclization, we prepared two types of furoylanilides (3 and 4) for their irradiation. In cases of furoylanilides (3 and 4), the presence of an ortho-ester group (3 and 4,X=COOMe) suppressed the photocyclization. The unsubstituted anilide (3,X=H) underwent photocyclization only under oxidative condition to give the lactam (11)[5]. However, the ortho-carboxyanilide (3,X=COOH) afforded three different types of the photocyclized products (12, 13, and 14) and their structures were deduced from the following spectral data [(12); i.r.; ν 1660 (NCO), n.m.r.; δ 7.50-6.80 (4H, m, arom.H), 6,45 (1H, t, J=2,5Hz, 2-H), 5.12 (1H, t, J=2.5Hz, 1-H), 5.10 (1H, d, J=10.5Hz, 3a-H), 4.48 (1H, dt, J=10.5, 2.5Hz, 9b-H). (13); i.r.; ν 1710(CHO), 1660 (NCO), n.m.r.; δ 9.03 (1H, d, J=5.5Hz, CHO), 7.60-6.95 (4H, s, arom.H), 3.50-2.20 (3H, ABC-type, 1-H, 1a-H, and 7b-H).



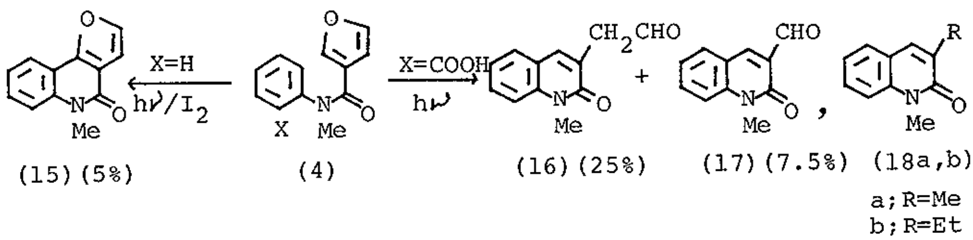
(5) (30%) (1) (6) (33%) (7) (10%)



(8) (45%) (2) (9) (28%) (10) (22%)



(11) (29%) (3) (12) (5%) (13) (10%) (14) (10%)



(15) (5%) (4) (16) (25%) (17) (7.5%) (18a,b)

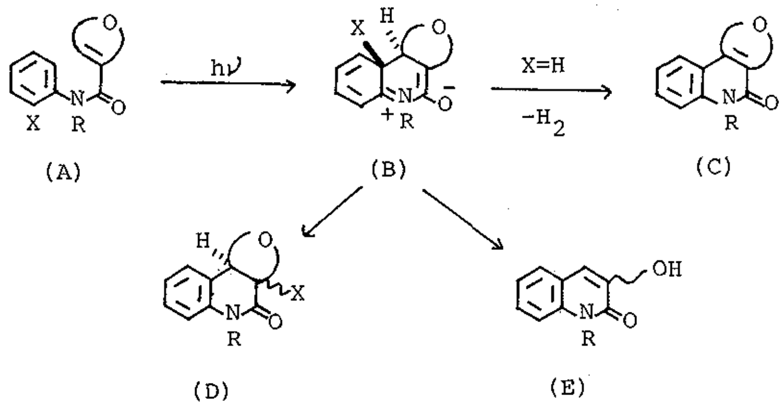
a; R=Me
b; R=Et

(14); i.r.; ν 1705 (CHO), 1660 (NCO), n.m.r.; δ 10.55 (1H, d, J=3.5Hz, CHO), 7.65-6.90 (4H, m, arom.H), 3.17 and 2.97 (each 1H, dd, J=8, 3.5Hz, 1a-H, and 7b-H), and 2.05 (1H, q, J=3,5Hz, 1-H)]. The lactams (13 and 14) were also photochemically formed from the lactam (12) upon irradiation, presumably as a result of the well-known photo-induced transposition of the dihydrofuran moiety (12)[6].

On the other hand, the photochemical reaction of β-furoyl-anilides (4) proceeded quite differently from those observed in cases of the α-isomers (3).

The unsubstitued anilide (4,X=H) underwent photocyclization only under oxidative condition to give the aromatic lactam (15)[3]. However, the photocyclization of the ortho-carboxyanilide (4, X=COOH) yielded two photocyclized lactams (16 and 17) whose structures were deduced first from their spectral data [(16); i.r.; ν 1730 (CHO), 1650 (NCO), n.m.r.; δ 9.83 (1H, t, J=2Hz, CHO), 7.80-7.20 (5H, m, arom.H), 3.80 (2H, d, J=2Hz, $C\underline{H}_2CHO$), and (17); i.r.; ν 1690 (CHO), 1645 (NCO), n.m.r.; δ 10.52 (1H, s, CHO), 8.37 (1H, s, 4-H), 8.00-7.05 (4H, m, arom,H)] and then confirmed by their conversions into the corresponding alkyl derivatives (18 a and b)[7] upon the Wolff-Kishner reduction.

These photochemical transformations including photocyclization of heterocyclic anilides described here would be explained as follows; a photocyclization would take place in the excited state of the anilide (A), which is a conjugated 6π-electron congener, to form a common cyclized intermediate (B), from which would afford



the respective products, for example, the dehydrolactam (C) upon dehydrogenolysis in the presence of an oxidizing agent, the lactam (D) upon simultaneous decarboxylation or migration of the substituent under non-oxidative condition, and the lactam (E) upon cleavage of the heterocyclic ring in the presence of oxygen function at the position where cyclization takes place.

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Received, 24th May, 1978