Non-oxidative Photocyclizations of Alkyl-substituted Acrylic Acid Anilides to Dihydrocarbostyrils

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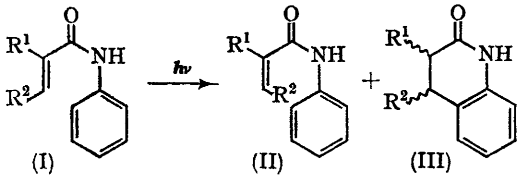
OXIDATIVE cyclizations of *cis*-stilbenes and related systems containing hetero-atoms are well-known.[1] Analogous oxidative cyclizations of diphenylamine,[2] benzoic acid anilide,[3] and aromatic Schiff bases[4] have also been reported. Non-oxidative cyclizations involving aromatic rings are much less common. Available examples are limited to stilbenes with strongly electronegative substituents in the 9,10-positions[5] and 2-biphenylisocyanate.[6]

During our study of the photochemistry of unsaturated acids and their derivatives,[7,8] we noted a non-oxidative cyclization of alkyl-substituted acrylanilides to alkyl-substituted 3,4-dihydrocarbostyrils. Irradiation of the anilides was carried out in ether solutions containing a small amount of acetic acid using a Pyrex immersion well and a Hanovia Type A 550 w mercury arc lamp. The reaction mixtures were separated into basic, neutral, and acidic fractions. The neutral fractions were crystallized directly or chromatographed on silica gel.

Irradiation of tiglic acid anilide (Ia) for 6 hr. gave angelic acid anilide (II, 16%) and a mixture of *cis*- and *trans*-3,4-dihydro-3,4-dimethylcarbostyril (IIIa, 58%). Sublimation (115°/0·03 mm.) of the mixture of stereoisomers gave a single isomer (probably *trans*), m.p. 115°, which was identical in infrared absorption to a sample of 3,4-dihydro-3,4-dimethylcarbostyril synthesized by another procedure.[9] Angelic acid anilide was identified by infrared comparison with an authentic sample.

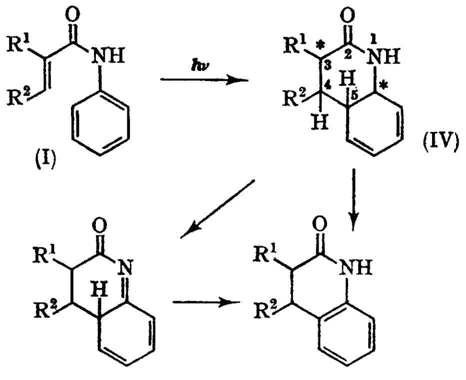


a: $R^1=R^2=Me$; b: $R^1=H$, $R^2=Me$; c: $R^1=Me$, $R^2=H$

Irradiation of *trans*-crotonic acid anilide (Ib) for five days gave a mixture of *trans*- and *cis*-crotonic acid anilides and 3,4-dihydro-4-methylcarbostyril (IIIb, 25%), m.p. 100–102° (lit.,[10] 98°). The product had the correct mass spectrometric molecular weight (161) and showed lactam carbonyl absorption at 6·04 μ. The n.m.r. spectrum showed aromatic protons (δ 7·0, m, 4H), N–H (δ 10·4, 1H), three aliphatic protons (δ 3·3–2·0, m). and methyl protons (δ 1·3, d, 3H).

α-Methylacrylic acid anilide (Ic) on irradiation for 9 hr. gave recovered starting material (39%) and 3,4-dihydro-3-methylcarbostyril (IIIc, 50%), m.p. 131° (lit.,[11] 130°). The yield based on unrecovered starting material is 82%. The product had the expected molecular weight (161) and infrared carbonyl absorption (6·04 μ). The n.m.r. spectrum showed aromatic protons (δ 7·0, m, 4H), N–H (δ 9·7, 1H), three aliphatic protons (δ 3·3—2·3, m, 3H), and methyl protons (δ 1·25, d, 3H).

The cyclization of (I) to (III) requires a hydrogen transfer which presumably occurs in an intermediate such as (IV). In principle three separate processes may be considered for the hydrogen transfer. A sequence of 1,2-hydrogen shifts (from 4 to 3 followed by 5 to 4) might occur, and, two 1,3-transfers from 5 to 3 and from 1 to 3 are possible. These paths can be distinguished by appropriate deuterium labelling experiments.



* = ·, +, or −

Irradiation of $[2,4,6\text{-}^2H_3]$tiglic acid anilide gave (IIIa) which contained deuterium at C-3. Some deuterium is lost in the irradiation. The loss presumably involves successive hydrogen transfer from 1 to 3 then 5 to 1 followed by exchange during work-up. Deuterium at position 1 is lost during work-up. Irradiation of *N*-deuterio-(Ia) in ether also gave (IIIa) which contained deuterium in the 3-position, the latter can be removed by treatment with sodium methoxide in methanol. A sequeuce of 1,2-hydrogen transfers is excluded by the labelling experiments. The 1,3-hydrogen transfers both occur to a significant extent.

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[1] F. Stermitz in, "Organic Photochemistry", ed. O. L. Chapman, Marcel Dekker, 1967, Vol. I, p. 247.

[2] E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc.*, 1963, 202; K. H. Grellmann, G. M. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, 1963, **85**, 1881; H. Linschitz and K. H. Grellmann, *ibid.*, 1964, **86**, 303.

[3] B. S. Thyagarajan, N. Kharasch, H. B. Lewis, and W. Wolf, *Chem. Comm.*, 1967, 615.

[4] K. H. Grellmann and E. Tauer, *Tetrahedron Letters*, 1967, 1909.

[5] M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, 1963, **85**, 2186; *J. Chem. Soc.*, 1964, 5544.

[6] J. S. Swenton, *Tetrahedron Letters*, 1967, 2855.

[7] A. W. Bradshaw and O. L. Chapman, *J. Amer. Chem. Soc.*, 1967, **89**, 2372.

[8] O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, 1967, **89**, 4243.

[9] S. Plant and R. Rosser, *J. Chem. Soc.*, 1930, 2444.

[10] F. Mayer, L. van Zütphen, H. Philipps, *Ber.*, 1927, **60**, 858.

[11] O. Mumm and H. Ludwig, *Annalen*, 1934, **514**, 34.