Photo-rearrangement of o-Nitrobenzanilide

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Summary o-Nitrobenzanilide rearranges to 2-(2-hydroxyphenylazo)benzoic acid *via* an intermediate azoxybenzene derivative under the influence of light.

SUBSTITUENT interactions in *ortho*-substituted nitroarenes have been promoted thermally, photochemically, and by acids and bases;[1,2] cyclised and uncyclised products are frequently encountered. The recently reported base-catalysed transformations of *NN*-disubstituted *o*-nitrobenzamides[3] prompts us to report our results on the photolysis of *o*-nitrobenzanilide.

Cream crystals of the anilide (1) turn maroon on exposure to ambient light, and an ethanol solution of the amide rapidly develops a blackcurrant colour when irradiated with an unfiltered 100w medium-pressure arc. The maroon photoproduct from the solution photolysis (15% yield after 12 h)‡ was identical to that from the light-exposed crystals, and had a visible, i.r., n.m.r., and mass spectrum consistent with structure (3); in agreement, on catalytic hydrogenation it afforded only anthranilic acid and *o*-aminophenol. Although azo- and azoxy-compounds have been isolated from the photolysis of *ortho*-nitro-

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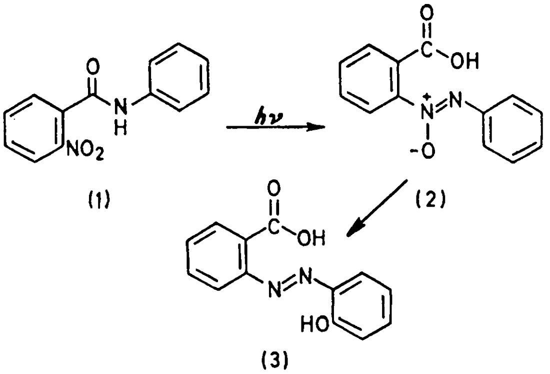
‡ Starting material (80%) was also recovered.

compounds, their formation in most cases can be attributed to bimolecular reactions involving reduction products.[4] The formation of the azo-derivative (3), on the other hand, is unusual in that a unimolecular process seems to be involved.

We suggest that this isomerisation is initiated by abstraction of the amide N–H proton by the excited nitro-group,[5] and proceeds to yield the azoxy-intermediate (2); further rearrangement of the azoxy-derivative to the final product (3) is in accord with the known photochemical azoxybenzene–hydroxyazobenzene rearrangement[6] in which the oxygen atom always migrates to the *ortho*-position of the aryl group more distant from the N–O function.[7] In support of this suggestion, the azoxybenzene (2) was detected (t.l.c.) in the photolysate, and a prepared sample[8] was quantitatively converted into the hydroxyazobenzene isomer (3) in a separate photolysis.

This appears to be a general reaction of *N*-aryl-2-nitrobenzamides. For example, the 2-nitrobenzoyl derivative of α-naphthylamine rearranges to 2-(2-hydroxy-1-naphthylazo)benzoic acid in both crystal and solution phases. Of greater interest is the analogous rearrangement of 2-nitrobenz-*o*-toluidide, since this toluidide has been isolated as a metabolite of the currently-abused hypnotic, Methaqualone.[9] It is possible that the intense colour formed on photolysis of the toluidide could form the basis of a sensitive colour test to identify the Methaqualone metabolite in urine.



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