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PHOTOCONVERSION OF 2,2'-DINITRODIPHENYLMETHANES TO 3-(2-NITROPHENYL) 2,1-BENZISOXAZOLES

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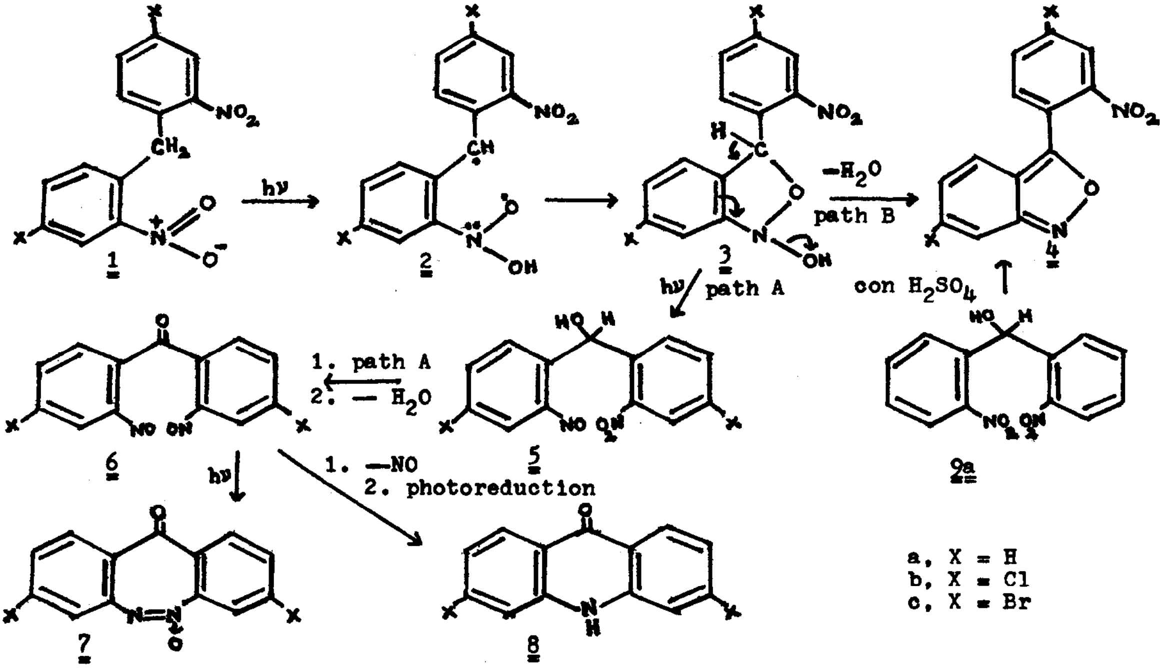
In a recent communication[1] we have reported the photoconversion of 2,2'-dinitrodiphenylmethanes (1) in isopropanol to 11-oxo-11H-dibenzo[c,f][1,2]diazepine-5-oxides (7) and acridones (8). The reaction was envisaged to proceed via the intermediate 6 formed by two successive oxygen insertion reactions involving both nitro groups in 1. Here we wish to report an interesting observation made by photolysing 1 in presence of a little H_2SO_4 in the reaction medium. The irradiation of 1 in ethanolic H_2SO_4 led to the preferential cyclisation of one of the nitro groups into the methylene group resulting in the formation of 3-(2-nitrophenyl)2,1-benzisoxazoles (4) (45-50% yield, corrected to recovered 1), instead of the coupling between nitrogens which occurs in the absence of H_2SO_4.

In a typical run a solution of 1.5g of 1a in 950ml of ethanol containing 2 ml of 98% H_2SO_4 was irradiated for 20h using a Philips HPK 125W high pressure mercury-quartz lamp. The photolysed solution after chromatography on an alumina column afforded in addition to the unchanged 1a (30%), 4a (35%)[m.p. 117-118°; M^+224; λ_{max}(EtOH), 323 nm; ν_{-NO_2}(KBr) 1540, 1360 cm^{-1}; n.m.r, a complex multiplet of aromatic protons, τ 1.7-3.2], the N-oxide 7a (6%), acridone 8a (4%) and 2,2'-dinitrobenzophenone (3%). The structure of 4a was confirmed by an alternate synthesis from 2,2'-dinitrodiphenyl carbinol (9a)[2] by treating with conc H_2SO_4, a procedure recently adopted for the preparation of 3-phenyl-2,1-benzisoxazole[3]. The yield of 4a obtained compared to the photochemical method was very low.

The generality of this interesting photoreaction was confirmed by similar conversions of the dichloro and dibromo analogs, 1b and 1c to 4b (m.p. 189°) and 4c (m.p. 207°) in ca 45% yields. 4b and 4c showed closely similar spectral data to those of 4a. The essential role of the acid in this photocyclisation was confirmed by the observation that the irradiation of 1 in 95% ethanol does not lead to the formation of 4 and proceeds exactly similar to the photolysis of 1 in isopropanol. A plausible mechanism to account our observations is outlined below.



During the photolyses of 1 in isopropanol or in ethanolic H_2SO_4 the abstraction of benzylic hydrogen by the electronically excited nitrogroup occurs first to form the biradical 2 which cyclises to the intermediate 3. 3 in presence of H_2SO_4 undergoes mainly dehydration to 4 (path B) and in the absence of H_2SO_4 completely rearranges (path A)[4] to the nitroso intermediate 5 which readily undergoes one more oxygen insertion process (path A) resulting in 6. 6 accounts for the formation of 7 and 8.[1]

Our observation, in addition to its mechanistic interest, provides a novel and easy method for the synthesis of 3-(2-nitrophenyl)2,1-benzisoxazoles. Further investigations to extend the method as a general route to 2,1-benzisoxazoles and related compounds are now in progress.

References:

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