Photolysis of *N*-Aryl-2-nitrobenzhydrazonoyl Bromides[1]; A Photochemical Formation of 3-Aryl-4-oxo-3,4-dihydro-1,2,3-benzotriazines

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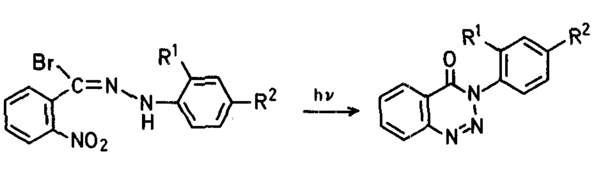
In continuation of our study on the photolysis of 2-nitrobenzaldehyde hydrazone derivatives[2,3], the photochemical behaviour of *N*-aryl-2-benzhydrazonoyl bromides **1** was investigated.

The observed photoreaction provides a new example of the formation of 3-aryl-4-oxo-3,4-dihydro-1,2,3-benzotriazines **2** which involves photodeoxygenation of the 2-aryl-4-oxidobenzotriazinium 1-oxide **6** and subsequent photoisomerization of the 2-aryl-4-oxidobenzotriazinium compound **7**. The present photoreaction promises to be widely applicable for the preparation of various 3-aryl-4-oxo-3,4-dihydro-1,2,3-benzotriazines.

The hydrazonoyl bromides **1a–c**[4] in acetonitrile were irradiated with a high-pressure mercury lamp through a Pyrex filter under nitrogen until the disappearance of **1a–c** was complete. The reaction mixture was chromatographed to isolate the benzotriazinones **2a–c** in 40–55 % yields, respectively. The presence of a small amount of some unidentified products in the reaction mixture was detected by thin-layer chromatography. The structures of **2a–c** were fully supported by microanalytical results and spectral data. The *p*-nitrophenyl derivative **2a** thus obtained was identical in every respect with a sample prepared by the previously reported method[5].

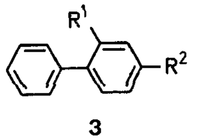
Employment of benzene as a solvent instead of acetonitrile resulted in the formation of the corresponding biphenyl derivatives **3a–c** in 5–10 % yield in addition to **2a–c** in 30–40 % yield.

The photofragmentation of 3-phenylbenzotriazinone (**2**, R^1, R^2 = H) accompanied with loss of nitrogen has been extensively studied[6]. On irradiation of **2a–c** for 3 h under the conditions employed, however, no appreciable gas evolution was observed and **2a–c** were recovered unchanged.



1 a-c **2 a-c**

	R1	R2
a	H	NO2
b	Br	CH3
c	Br	Br



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Scheme A

Treatment of the hydrazonoyl bromides **1** with base[4] causes their conversion into a class of *N*-phenyl-heterocycle *N*-oxides, which has been the subject of uncertainty and controversy[4,7]. More recently, some evidence supporting the betaine *N*-oxide structure **6** rather than the anthranil *N*-oxide structure **4**[8,9] has been presented.

Under analogous conditions, the betaine *N*-oxide and betaine, **6** and **7**[8,9] prepared independently, also gave the benzotriazinone **2**. The betaine *N*-oxide **6** was isolated after a short period irradiation of **1**.

Thus, the present photoreaction can be rationalised in terms of the intermediacy of **6** and **7** as shown in Scheme **B**.

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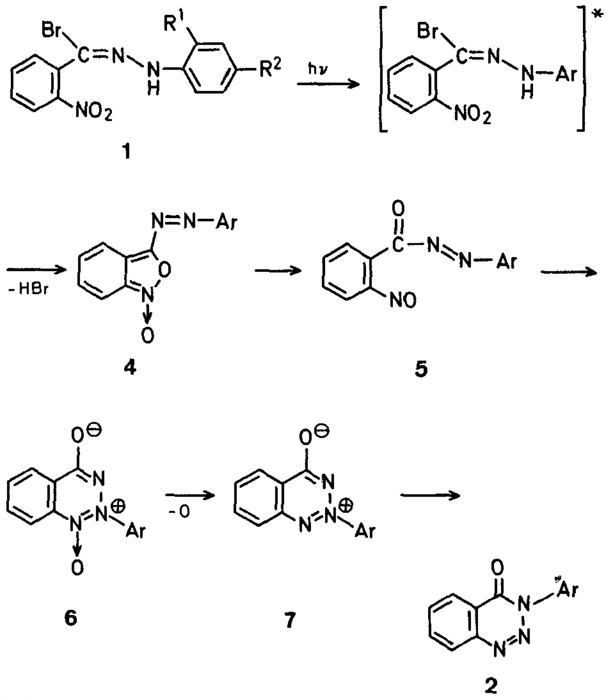
Table. Preparation of 3-Aryl-4-oxo-3,4-dihydro-1,2,3-benzotriazines **2a–c**

Product	Reaction time	Yield [%]	m.p. (Lit. m.p.)	Molecular formula[a]	M.S. *m/e* (M^+)
2a	5 h	40	255° (254°)[5]	$C_{13}H_8N_4O_3$ (268.2)	268
2b	5 h	50	186°	$C_{14}H_{10}BrN_3O$ (316.2)	316
2c	5 h	55	140° (136°)[5]	$C_{13}H_{17}Br_2N_3O$ (381.2)	381

[a] All products gave satisfactory microanalyses (C ±0.10 %, H ±0.10 %, N ±0.15 %).



Scheme **B**

The betaine *N*-oxide **6** appears to be produced via the anthranil *N*-oxide **4** and its open-chain nitroso isomer **5**[8]. The formation of the biphenyls **3** in the photolysis of **1** in benzene may be ascribed to the trapping of phenyl radicals generating partly by photo-fragmentation of the transient intermediates **4** and **5**.

The detail mechanism is not clear at present and further studies are now in progress.

Preparation of 3-Aryl-4-oxo-3,4-dihydro-1,2,3-benzotriazines 2a–c; General Procedure:

To the *o*-nitrobenzaldehyde *p*-nitrophenylhydrazone (0.01 mol) suspended in glacial acetic acid (100 ml), bromine (0.01 mol) in acetic acid (10 ml) is added dropwise with vigorous stirring at room temperature. The resultant yellow solid is collected, washed well with water, and recrystallised from acetone to give the hydrazonoyl bromide **1a**; yield: 55%; m.p. 145°.

The other hydrazonoyl bromides (**1b** and **1c**) are prepared[4] analogously; yields: 50%, 60%; m.p. 104°, 110°, respectively.

The *N*-aryl-2-nitrobenzhydrazonoyl bromides **1a–c** thus obtained (5 mmol) in acetonitrile (200 ml) are irradiated with a 400 W high-pressure mercury lamp under nitrogen through a Pyrex filter. After irradiation for 5 h, the solution is chromatographed on a silica gel column (chloroform as eluent) and the product recrystallised from ethanol to give the 3-aryl-4-oxo-3,4-dihydro-1,2,3-benzotriazines **2a–c**.

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