

4-Azidoquinoline N-Oxide: Synthesis and Photolysis

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Received June 20, 2007

Abstract—In photolysis of 4-azidoquinoline N-oxide azoxy compound was isolated as the final reaction product. This result may be ascribed to the dimerization of the intermediate nitrene to azo compound followed by oxidation of the latter with air oxygen. The initially arising nitrene is stabilized by resonance conjugation involving the aromatic system and the N-oxide group. The rate constants of 4-azidoquinoline N-oxide photolysis were measured in various solvents and the values of spin density and bond lengths in the formed nitrene were calculated.

DOI: 10.1134/S1070428008050163

The decomposition of organic azides with liberation of a nitrogen molecule can be performed by photolysis or thermolysis. The first way is obviously preferable for aryl azides for they possess adsorption bands in the long-wave region of the spectrum thus making possible their photolysis without affecting the other chromophores present in the molecule.

The photodecomposition of aryl-substituted azides is known to produce nitrenes whose stabilization may occur intramolecularly: As a result of conversion into azirine followed by electrocyclic cycle opening and transformation into azepine [1]. However relatively stable nitrenes are prone to dimerization even in the presence of “nitrene traps” [1–3]. It should be also considered that under the UV irradiation the heteroaromatic N-oxides are capable of various rearrangements [4, 5]. The ease of nitrogen ejection from the azide molecule can be strongly affected by the other functional groups present in the initial molecule. The unsubstituted quinoline N-oxide is known to be converted under the action of light along two routes, yielding 2-quinolone in hydroxy-containing solvents and in those containing no hydroxy groups, benzazepine, and a small amount of quinoline formed in both cases [6, 7].

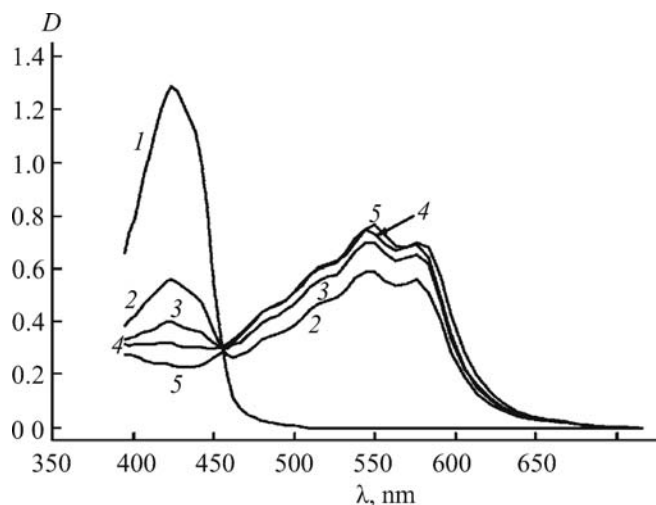
Yet in the case of aryl azides the photolysis can leave intact the other chromophore groups. Actually, 4-azidopyridine N-oxide was converted by photolysis not into an azo compound but to benzazirine and afterwards to dehydroazepine [8].

In the study of reactions in the dark of quinolines N-oxides we found that even in the presence of an azide group in the heteroaromatic framework these compounds reacted with active dipolarophiles, e.g., with dimethyl acetylenedicarboxylate, only involving the N-oxide function [9]. In this connection it was reasonable to investigate the behavior of this compound under the photolysis conditions. Just the investigation of photo-transformations of 4-azidoquinoline N-oxide was the target of this study.

Initial N-oxide (**I**) we synthesized in ~80% yield by a new simple procedure we had developed: 4-Nitroquinoline N-oxide was kept in solution with sodium azide in the dark for 2–3 days at room temperature. Previously compound **I** was prepared in 45% yield from the 4-chloroquinoline N-oxide and sodium azide at 115–125°C in a sealed ampule, and the 4-chloroquinoline N-oxide was synthesized from 4-nitroquinoline N-oxide and acetyl chloride [10].

Azide **I** was irradiated with UV light of >220 nm wavelength (through a quartz filter) in various solvents (concentration 1×10^{-4} – 5×10^{-3} mol l⁻¹). The progress of the photochemical reaction that proceeded for ~1 min was followed by registering the UV spectra every 5–10 s (see the figure).

Practically immediately after the start of irradiation of the N-oxide azide solution the color changed from yellow to bright red, and a settling of a dark-red crystalline precipitate was observed. Its elemental



Variations in electronic spectrum of a solution of 4-azidoquinoline *N*-oxide in acetone ($c\ 1.0 \times 10^{-4}\ \text{mol l}^{-1}$) under irradiation (1, 0 s; 2, 10 s; 3, 15 s; 4, 20 s; 5, spectrum of the final reaction product).

analysis and spectral characteristics testify to the structure of azoxy compound **III**. In the IR spectrum of the isolated substance recorded from the pellets with KBr the absorption bands of azide group at 2093 and 1300 cm^{-1} are lacking, but a new band appears at 1570 cm^{-1} . This band may be assigned to the stretching vibration of the N=N bond. In the spectrum a strong band at 1270 cm^{-1} is also present characteristic of vibrations of N → O group of the aromatic *N*-oxides.

The spectral characteristics and rate constants of the initial compound disappearance are given in Table 1.

The rate constant of disappearance of the initial azide was calculated from the variation of the optical density of its solutions at λ_{max} for various solvents:

$$k = (1/t)(1/c_{\text{initial}}) \left(\frac{D_{\text{initial}} - D_{\text{current}}}{D_{\text{current}}} \right),$$

where k is the rate constant of the reaction, t is the irradiation time, c_{initial} is the concentration of the initial

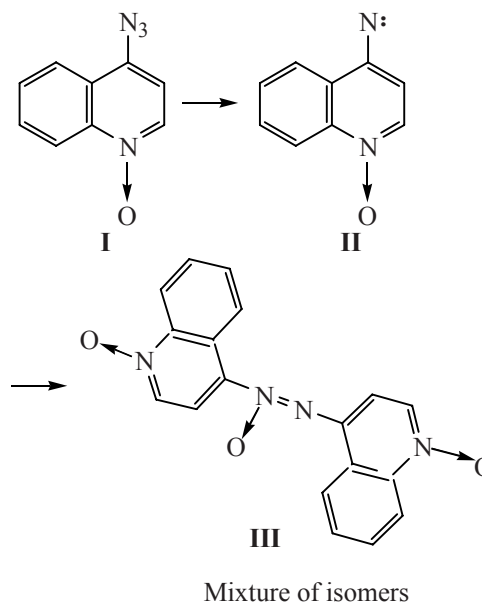
Table 1. Characteristics of irradiated solutions of 4-azidoquinoline *N*-oxide and constants of photolytic decomposition ($c \times 6.0 \cdot 10^{-3}\ \text{mol l}^{-1}$)

Solvent	λ_{max} , nm	ϵ , $\text{l mol}^{-1}\ \text{cm}^{-1}$	k , $\text{l mol}^{-1}\ \text{min}^{-1}$
Acetone	370	12000 ± 500	1058 ± 81
Acetonitrile	366	12400 ± 500	2462 ± 98
Benzene	374	13000 ± 500	1542 ± 226
Ethanol	354	15000 ± 500	802 ± 43

solution, D_{initial} is the optical density of the initial solution, D_{current} is the optical density at the given moment.

As seen from Table 1, the solvent character did not significantly affect the reaction rate.

For the preparative synthesis of azoxy compound **III** we carried out the photolysis of *N*-oxide **I** in acetone solution in a quartz cell under the sunlight.



The formation of azoxy compound may be represented by a Scheme assuming the intermediate formation of nitrene **II**.

To estimate the reactivity of the hypothetical nitrene **II** we calculated the values of spin density on each atom and the bond orders. Method RHF in the basis STO-6G was used in the calculations. Some calculated data are given in Table 2.

Table 2. Parameters of nitrene formed from 4-azidoquinoline *N*-oxide

Spin density					
O	N ^l	C ²	C ³	C ⁴	N (nitrene)
0.896	0.072	0.003	0.037	0.000	0.950
Bond length, Å (Bond order)					
O-N	N-C ²	C ² =C ³	C ³ -C ⁴	C ⁴ =N (nitrene)	
1.359 (1.125)	1.429 (1.008)	1.319 (1.835)	1.488 (1.028)	1.290 (1.883)	

Azides of aromatic compounds commonly have the spin density on the nitrene nitrogen about 2 [11], but the introduction of the N-oxide group essentially alters the situation. In the nitrene formed from 4-azidoquinoline N-oxide the spin density is distributed between the oxygen of the N-oxide group and the nitrene nitrogen atom; this fact apparently results in the nitrene stabilization.

The latter affects the nitrene reactivity. In particular, in the photolysis of N-oxide **I** in the presence of excess acrylonitrile or butyl vinyl ether only azoxy compound **III** was obtained, and no addition products of nitrene across the multiple bond were detected that could be ascribed to its low reactivity.

The formation under the experimental conditions of azoxy compound **III** is evidently due to the presence of oxygen both in the solvent and in the atmosphere of the reaction vessel.

Thus the photolysis of the bifunctional compound, 4-azidoquinoline N-oxide (**I**) did not involve directly the N-oxide group. However it played a significant part in distribution of the spin density in the primarily formed nitrene that was characterized by reduced activity. The main route of its transformation was dimerization followed by oxidation with the oxygen present in the reaction environment.

EXPERIMENTAL

The photolysis of 4-azidoquinoline N-oxide in various solvents was carried out in a quartz cell under the UV radiation of a mercury lamp of high pressure Q-139 of a power 250 W. The spectra in UV and visible regions and the variation in the intensity of absorption bands of solutions as a function of irradiation time were measured on a spectrophotometer Specord M40. IR spectra of the initial compounds and photolysis products were recorded on a Specord 75IR instrument.

4-Azidoquinoline N-oxide (I). To a solution of 0.38 g (2 mmol) of 4-nitroquinoline N-oxide in 3 ml of dioxane was added a solution of 0.14 g (2.2 mmol) of sodium azide in 1 ml of water and several drops of ethanol. The reaction mixture was left standing in the dark at room temperature for 2–3 days (TLC monitoring, eluent chloroform–ethanol, 10:1). The solvents were removed in a vacuum, 2 ml of water was added to the residue, the reaction product was extracted into

chloroform (2 × 5 ml). The extract was dried with anhydrous sodium sulfate, chloroform was removed in a vacuum, the residue was recrystallized from acetone. Yield 0.3 g (81%), mp 140–142°C (decomp.), light-sensitive. IR spectrum (1% solution in CHCl₃), ν , cm⁻¹: 2093 (asymmetric stretching vibrations of N₃), 1292 (N → O), 1318 (symmetric stretching vibrations of N₃). Electronic spectrum (in 96% ethanol), λ_{\max} , nm (log ϵ): 233 (4.31), 258 (3.96), 355 (3.88).

Photolysis of N-oxide I. A solution of 93 mg (0.5 mmol) of N-oxide **I** in 3 ml of acetone in a quartz cell was exposed to the sunlight for 8–10 min. On completion of the reaction (TLC monitoring, eluent acetone–hexane, 4:1) and at the end of nitrogen evolution the formed dark-red crystalline precipitate of azoxy compound **III** was filtered off, washed with ethyl ether, dried in air, and recrystallized from acetone. We obtained 58 mg (70%) of azoxy compound **III**, mp 278–280°C. Found, %: C 64.87; H 3.66; N 17.54. C₁₈H₁₂N₄O₃. Calculated, %: C 65.06; H 3.61; N 16.87. The sample obtained at photolysis of N-oxide **I** under irradiation with a mercury lamp was identical to the above described compound in the melting point and TLC data.

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