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Products of 6-Azidoquinoline Photooxidation: Thermal and Photochemical Routes of Nitroso Oxide Consumption

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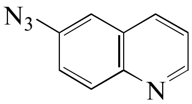
The photolysis of aryl azides in the presence of oxygen leads to the corresponding nitro and nitroso compounds [1, 2]. These products are considered to result from nitroso oxides (ArNOO), intermediate species formed in the reaction of molecular oxygen with triplet aromatic nitrenes [3].

In this work, we have studied the products of photooxidation of 6-azidoquinoline **1** in acetonitrile and showed that there are two reaction channels of consumption of nitroso oxide **2**: thermal and photochemical. The major thermal channel is the isomerization of the nitroso oxide with the opening of the aromatic ring, while the minor photochemical channel leads to formation of 6-nitroquinoline.



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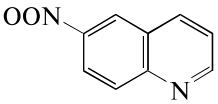

2

A solution of azide **1** (1×10^{-3} mol/L) in acetonitrile (75 mL) saturated with oxygen was photolyzed using filtered light (BS-4 light filter, $\lambda > 300$ nm) of a xenon lamp in a thermostated reactor at 20°C. The reaction was conducted until complete consumption of the azide. The reaction mixture was analyzed by reversed-phase HPLC (acetonitrile as a mobile phase). The chromatogram indicated the formation of three products (Fig. 1). The preparative separation of the mixture resulted in isolation of ~5 mg of product **3** (peak *1* on the chromatogram), ~1 mg of product **4** (peak *2*), and trace amounts of product **5** (peak *3*).

Product **3** is a green crystalline solid with a melting point of 200–202°C, whose UV spectrum in acetonitrile shows two strong absorption bands at 300 and 416 nm and a very weak band at 677 nm.

NMR spectra in CD_3CN (99.95% D) were recorded on a Bruker AV-500 spectrometer with TMS as a reference. The ^1H NMR spectrum of a solution of product **3** indicates that **3** is a mixture of two compounds, **3a** and **3b**, in a 1 : 2 ratio. The spectrum of the second compound is slightly shifted downfield relative to that of the first one, the number of protons in the first compound being exactly one half of that in the second one. As a whole, the ^1H NMR spectra of the two compounds are very similar. This also holds true for the ^{13}C NMR spectrum. The intensity ratio for matched signals is about 1 : 2, that is, the number of carbon atoms in the first compound is half the number in the second compound. This allows us to draw a conclusion that product **3** exists in solution in dimeric and monomeric forms.

From the analysis of the spectral data, we concluded that compound **3** is 3-nitrosoindolizine-8-carbaldehyde formed according to Scheme 1.

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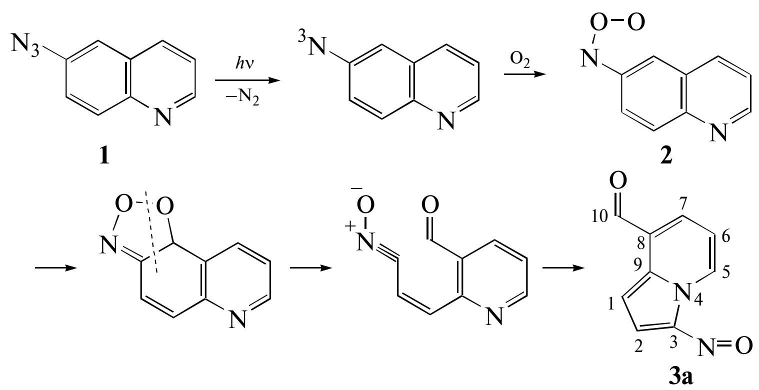
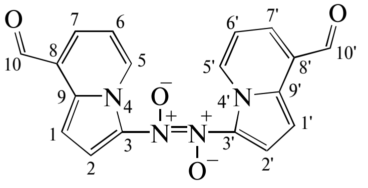


Scheme 1.

The terminal oxygen atom of the nitroso oxide group of compound **2** reacts at the *ortho* position of the aromatic ring to form a five-membered ring. The ring decomposes with cleavage of the C–O and O–O bonds, and the aromatic ring transforms into nitrile oxide, which is stabilized to form nitroso compound **3a**. It is known that nitroso compounds can dimerize [4]:



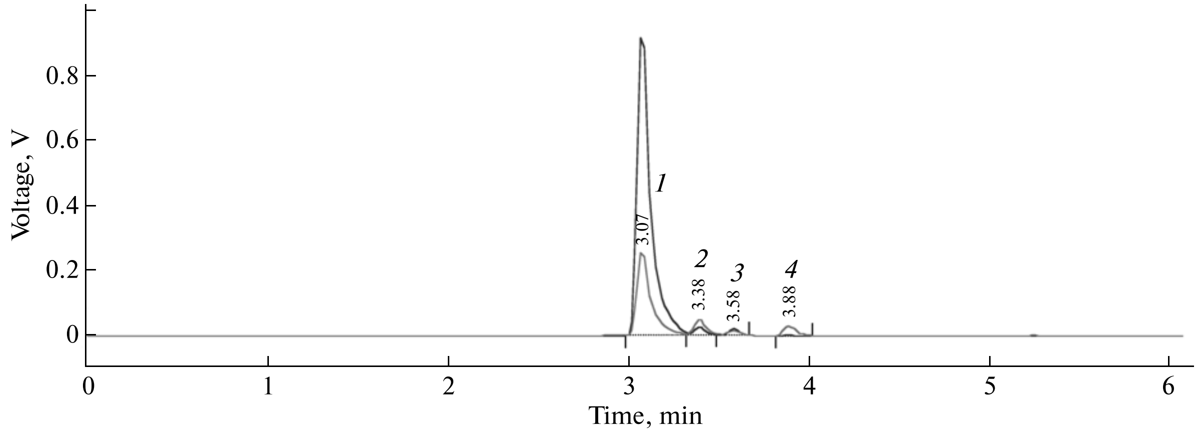
3b

Thus, the signal assignment in the ^{1}H NMR spectrum of dimer **3b** (500 MHz, CD$_3$CN, δ, ppm): 10.23 (s, 2H, C(10)H, C(10')H), 10.17 (dd, 2H, C(5)H, C(5')H, ^{3}J 7.1, ^{4}J 1.1), 8.42 (d, 2H, C(1)H, C(1')H, J 5.1), 8.27 (dd, 2H, C(7)H, C(7')H, ^{3}J 7.1, ^{4}J 1.1), 7.66 (d, 2H, C(2)H, C(2')H, J 5.1), 7.48 (t, 2H, C(6)H, C(6')H, J 7.1).

For monomer **3a** ^{1}H NMR (500 MHz, CD$_3$CN, δ, ppm): 10.19 (1H, C(10)H, 10.01 (dd, 1H, C(5)H, ^{3}J 7.1, ^{4}J 1.1), 7.47 (d, 1H, C(1)H, J 5.1), 8.26 (dd, 1H, C(7)H, ^{3}J 7.1, ^{4}J 1.1), 6.86 (d, 1H, C(2)H, J 5.1), 7.45 (t, 1H, C(6)H, J 7.1).

Signal assignment in the ^{13}C NMR spectrum of the dimer: 192.03 (C(10), C(10')), 156.31 (C(3), C(3')), 140.00 (C(7), C(7')), 135.40 (C(1), C(1')), 131.68 (C(10), C(10')), 156.31 (C(3), C(3')), 140.00 (C(7), C(7')), 135.40 (C(1), C(1')), 131.68 (C(5), C(5')), 128.25 (C(9), C(9')), 126.50 (C(8), C(8')), 120.45 (C(6), C(6')), 110.69 (C(2), C(2')). For the monomer ^{13}C NMR (CD$_3$CN, δ, ppm): 191.87 (C(10)), 162.01 (C(3)), 139.52 (C(7)), 109.70 (C(1)), 128.94 (C(5)), 135.84 (C(9)), 126.50 (C(8)), 117.36 (C(6)), 104.35 (C(2)).

The structure of compound **3** was confirmed by mass spectroscopy (TermoFinnigan MAT95XP). MS (EI, 70 eV, m/z (I_{rel}, %)): 174 [M]$^+$ (100), 144 [M–NO]$^+$ (32.5), 158 [M–O]$^+$ (8.2), 130 [M–O–CO]$^+$ (13.2), 116 [M–NO–CO]$^+$ (36.1), 89 [M–NO–CO–NCH]$^+$ (25.6).



Chromatogram of a reaction mixture obtained by the photolysis of a solution of 6-azidoquinoline in acetonitrile (1 × 10^{-3} mol/L) saturated with oxygen. Mobile phase is acetonitrile, detection wavelengths are 240 and 300 nm. *1*, product **3**; *2*, product **4**; *3*, product **5**; *4*, initial azide **1**.

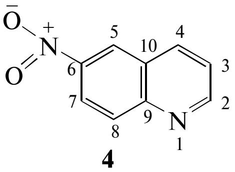
Table 1. The yield of products of photooxidation of 6-azidoquinoline in acetonitrile at 20°C

Photolytic source wavelength range, nm	$[\mathbf{1}]_0$, mol/L	Yield, % *	
		3	**4**
300–1000	1.07×10^{-4}	70	14
270–380	1.09×10^{-4}	84	4
300–380	1.03×10^{-4}	86	3
300–380	1.06×10^{-4}	95	4
300–380	1.08×10^{-4}	87	4

* Per consumed azide.

For $C_9H_6N_2O_2$ anal. calcd. (%): C, 62.07; H, 3.45; N, 16.09. Found (%): C, 61.72; H, 3.12; N, 15.36.

Compound **4** corresponding to the peak *2* in the HPLC chromatogram (figure) was identified by mass spectrometry as 6-nitroquinoline (CAS 613503), the similarity index for the library and recorded spectra was 93%. MS (EI, 70 eV, *m/z* (I_{rel}, %)): 174 $[M]^+$ (100), 144 $[M-NO]^+$ (6), 128 $[M-NO_2]^+$ (82).



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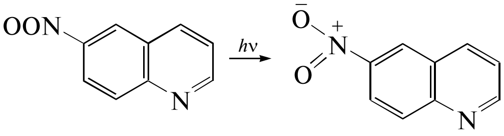
Compound **4**: ^1H NMR (500 MHz, CD_3CN, δ, ppm): 9.09 (dd, 1H, C(2)H, ^3J 4.2, ^4J 1.5), 8.91 (d, 1H, C(5)H, ^4J 2.5), 8.53 (d, 1H, C(4)H, *J* 8.3), 8.46 (dd, 1H, C(7)H, ^3J 9.3, ^4J 2.5), 8.21 (d, 1H, C(8)H, *J* 9.3), 7.68 (dd, 1H, C(3)H, *J* 8.3, ^4J 4.2).

We failed to identify compound **5** (peak *3* in the HPLC chromatogram (figure) isolated in trace amounts, only molecular ion of 298 was detected.

Thus, the major products of the photooxidation of 6-azidoquinoline are 3-nitrosoindolizine-8-carbaldehyde (**3**) (isolated yield ~37% toward the consumed azide) and 6-nitroquinoline (**4**) (~7%).

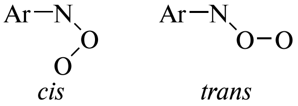
To elucidate the effect of wavelength of photolytic source on the yield of products of azide **1** photooxidation, we performed a quantitative analysis of reaction mixtures by HPLC without isolation of products (table). In this case, there is no loss of reaction products inevitable for preparative separation, and analysis results more adequately reflect the mechanism of the studied process. The reaction was carried out by irradiating solutions of compound **1** (~1×10^{-4} mol/L) in acetonitrile saturated with oxygen by filtered light of a xenon lamp using a BS-4 light filter (λ > 300 nm), an UFS-2 filter (270–380 nm), or their combination (300–380 nm) until complete consumption of the azide. The data of Table 1 show that the use of a narrow wavelength range for irradiation leads to a decrease in the yield of 6-nitroquinoline **4** and an increase in the yield of nitroso compound **3**. The absorption maximum of aromatic nitroso oxides is known to be, as a rule, in the long-wavelength spectral region (λ_{max} > 400 nm) [5]. Therefore, our results indicate the photochemical origin of formation of $ArNO_2$ from ArNOO:



This reaction is likely to proceed through the formation of cyclic isomer of nitroso oxide **2**, dioxaziridine.

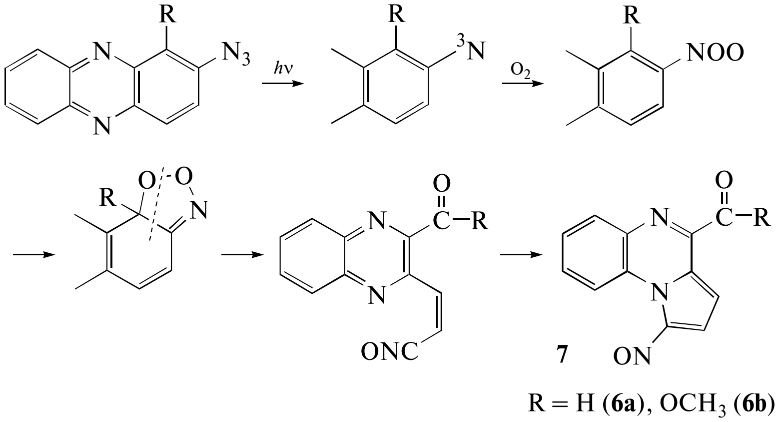
The isomerization of nitroso oxides with cleavage of the aromatic ring (Scheme 1) proceeds under mild thermal conditions and constitutes the main reaction channel of consumption of these species.

The N–O sesquibond in the nitroso oxide molecule [6] causes their existence as *cis* and *trans* isomers.



Only the *cis* isomer of the nitroso oxide can react at the *ortho* position of the aromatic ring. The high yield of substance **3** (table) indicates that it is a product of transformation of both isomeric forms. In this case, the *trans* form has to isomerize first into the *cis* form (Scheme 1), which undergoes further transformations to give finally product **3**.

In [7], the authors revealed that the photolysis of phenazines **6a** and **6b** in the presence of oxygen in benzene produced nitroso compound **7** in 57 and 42% yields, respectively. To explain the formation of **7**, the authors suggested Scheme 2, which is similar to Scheme 1.



Scheme 2.

The work [7] was unnoticed by the specialists who study nitroso oxides [3] and the corresponding nitro- and nitrosobenzenes are still believed to be the main transformation products of these species. In the present study, we confirmed the results obtained in [7] and showed that the main route of consumption of nitroso oxides is the thermal reaction channel that implies the intramolecular reaction of the NOO group with the *ortho* position of the aromatic ring as the first stage. Nitrobenzene can form from nitroso oxide only upon photoexcitation of the latter.

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