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CHEMISTRY

Redox Isomerization of Aromatic Nitroso Oxides

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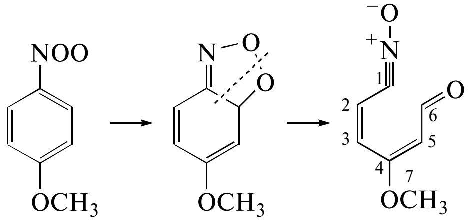
The reaction of triplet aromatic nitrenes with molecular oxygen leads to nitroso oxides ArNOO, labile species that are intermediates of photooxidation of aromatic azides [1] and deoxygenation of aromatic nitroso compounds with trivalent phosphorus compounds (phosphines and phosphites) in the presence of oxygen [2]. In the course of the photooxidation of aromatic azides, nitroso oxides are believed to produce corresponding nitro- and nitrosobenzenes [3, 4].

We have revealed in this study that nitroso oxides are consumed under conditions of thermal activation and undergo an unusual isomerization reaction. It was shown previously by flash photolysis [5] that the consumption of ArNOO follows a first-order kinetics. The reaction proceeds thermally because, under conditions of flash photolysis, exposure time is several orders of magnitude shorter than the lifetime of nitroso oxides (~0.005 to 10 s [5]). This work deals with the elucidation of the nature of this reaction. 4-Methoxyphenylnitroso oxide was studied as an example.

We analyzed a reaction mixture obtained on exposure of an acetonitrile solution of 4-methoxyphenyl azide (5×10^{-4} M) to one 50-μs light pulse (270–380 nm) with an energy of 400 kJ in the presence of oxygen using reversed-phase HPLC (mobile phase is acetonitrile or acetonitrile–water (70 : 30)) (Fig. 1). The main reaction products were found to be compound **X** and 4,4'-dimethoxyazobenzene (identified by comparison with an authentic sample). Dimethoxyazobenzene results from the recombination of triplet nitrenes or their reaction with the initial azide. The comparison with authentic samples showed that compound **X** is neither nitro- nor nitrosobenzene. These compounds were absent in the reaction mixture. We managed to obtain ~3 mg of compound **X**, which slowly decomposes when exposed to light in an acetonitrile solution at ambient temperature but stable for several weeks upon storage in a freezing chamber.

The UV spectrum of the isolated compound shows a maximum at 300 nm (Fig. 2). The IR spectrum exhibits an intense band in the region of stretching vibrations of triple bonds (2295 cm^{-1}). The ^1H NMR spectrum of compound **X** in CD_3CN displays four doublets with the following chemical shifts (δ, ppm, J, Hz): 9.90 (1H, J = 7.3), 7.42 (1H, J = 11.3), 5.95 (1H, J = 11.3), 5.60 (1H, J = 7.3), and a singlet at 3.82 ppm (3H). The ^{13}C NMR spectrum shows signals at 189.92, 167.59, 134.80, 121.57, 108.26, 105.29, and 57.44 ppm. From the analysis of spectral data, we drew a conclusion that compound **X** is 4-methoxy-6-oxohexa-2,4-dienylnitrile oxide (**1**) formed according to Scheme 1.



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Scheme 1.

The terminal oxygen atom of the nitroso oxide group interacts with the *ortho*-position of the benzene ring to give a five-membered ring. The ring undergoes opening with the cleavage of C–C and O–O bonds so that to the aromatic ring transforms into a conjugated diene with the aldehyde and nitrile oxide functional groups at the termini of the molecule. Such a transformation may be considered a redox isomerization of nitroso oxides.

Signal assignment in the ^1H NMR spectrum is as follows (δ, ppm): 9.90 (C-6), 7.42 (C-3), 5.95 (C-2), 5.60 (C-5), 3.82 (C-7). ^{13}C NMR (δ, ppm): 189.92 (C-6), 167.59 (C-4), 134.80 (C-3), 121.57 (C-1), 108.26 (C-2), 105.29 (C-5), 57.44 (C-7). On the basis

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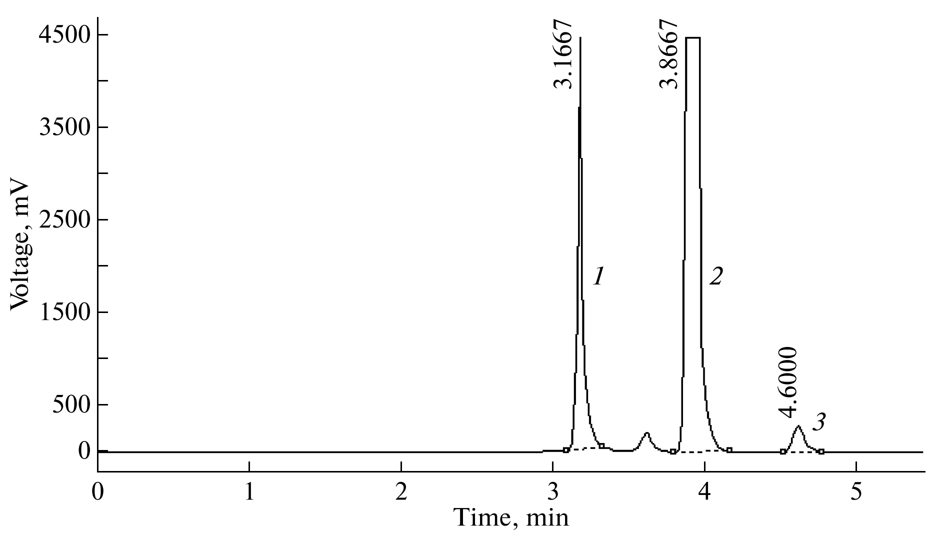


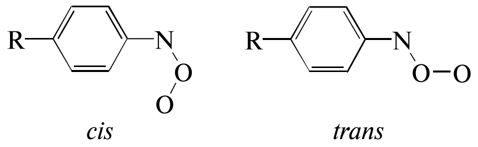
Fig. 1. Chromatogram of the concentrated reaction mixture obtained by the flash photolysis of a solution of 4-methoxyphenyl azide in acetonitrile (5×10^{-4} mol L^{-1}) saturated with oxygen.

Mobile phase is acetonitrile, detection wavelength is 300 nm. Components: (*1*) **X** , (*2*) 4-methoxyphenyl azide, and (*3*) 4,4'-dimethoxyazobenzene.

of the spin–spin coupling constants in the ^{1}H NMR spectrum between the protons at (C-2) and (C-3) (11.3 Hz), one can draw a conclusion that the double bond between these carbon atoms has the *cis* configuration. Calculation with the use of increments [6] indicates that the C(4)=C(5) bond also has *cis* configuration because, in the case of *trans* configuration, the resonances of C(4) and C(5) should appear downfield: at 171.0 and 107.6 ppm, respectively. The band in the IR spectrum at 2295 cm^{-1} corresponds to the stretching vibrations of C≡N bond in the nitrile oxide group. Its position agrees well with the position of the corresponding band in the IR spectrum of nitrile oxide stabilized on a polymeric support (2296 cm^{-1}) [7].

Compound **1** oxidizes triphenylphosphine to triphenylphosphine oxide. Trivalent phosphorus compounds are known to reduce nitrile oxides into corresponding nitriles [8]. The concentration of compound **1** was determined from the concentration of Ph_3PO resulting from the addition of Ph_3P to a solution of compound **1** (table, run 1). Compound **1** was completely consumed over the reaction time to give a new compound slightly more polar than **1** judging from the retention time. It is obvious that this compound is the corresponding nitrile. The extinction coefficient at absorption maximum (λ = 300 nm) of compound **1** in acetonitrile was assessed to be $\varepsilon \sim 2 \times 10^4$ L mol^{-1} cm^{-1}. The yield of intermediate nitroso oxide over one light pulse per consumed azide was determined from the concentration of compound **1** (table, run 2). It is ~40%, while the yield of azobenzene is ~25%. Taking into account that azobenzene results from two molecules of triplet nitrene, the total yield of triplet nitrene per consumed azide is ~90%.

The one-and-a-half N–O bond in nitroso oxide molecules [9] causes their existence as *cis* and *trans* isomers.



Scheme 2.

The oxygen atom of only *cis* isomer of the nitroso oxide can react at the *ortho* position of the benzene

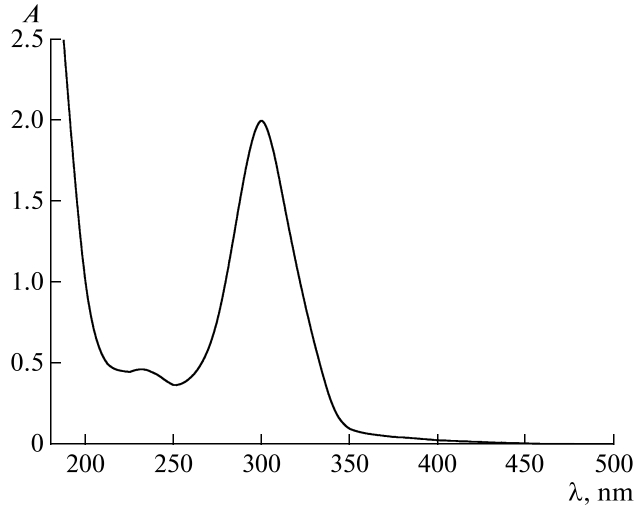


Fig. 2. UV spectrum of compound *X* in acetonitrile.

The results of analysis of the composition of different reaction mixtures

Run no.	[Initial reactants] × 10^4, mol L^{-1}				[Products] × 10^4, mol L^{-1}			
	$[ArN_3]$ $(\Delta[ArN_3])$	[**1**]	[ArNO]	$[Ph_3P]$	[**1**]	[ArN=NAr]	$[Ph_3PO]$	[ArNO]
1	–	0.16	–	1.0	–	–	0.16	–
2	5.0 (0.47)	–	–	–	0.19 [40%]	0.12 [25%]	–	–
3	5.0 (0.33)	–	–	1.0	0.05 [15%]	0.07	0.08 [24%]	0.08 [24%]

Note: Acetonitrile was used as a solvent, 295 K. The concentration of consumed azide is given in parentheses, and the yield of products is presented in square brackets. The concentration of compound **1** was determined from the yield of the phosphine oxide. Reaction time is 19 h.

ring. We show below that compound **1** results from the transformation of both isomeric forms. The *trans* form initially undergoes isomerization to the *cis* isomer (rate constant at 295 K in acetonitrile $k_{iso} = 0.37 \pm 0.02\ s^{-1}$ [5]), which, in turn, transforms into nitrile oxide ($k_{iso} = 11.3 \pm 0.2\ s^{-1}$ [5]).

We demonstrated recently that the *cis* and *trans* isomers of arylnitroso oxide show different reactivity both in the monomolecular consumption reaction [5] and toward organic substrates [10, 11]. Only *trans* isomer reacts with triphenylphosphine, whereas *cis* isomer undergoes monomolecular consumption [11]. The flash photolysis of 4-methoxyphenyl azide in the presence of Ph_3P (1×10^{-4} mol L^{-1}) led to a considerable decrease in the concentration of nitrile oxide **1** (table, runs 3 and 2) and to the emergence of triphenylphosphine oxide and 4-methoxynitrosobenzene in the reaction mixture, which resulted from the reaction of *trans* nitroso oxide and triphenylphosphine. The rate constant for the reaction of *trans*-4-methoxyphenylnitroso oxide with triphenylphosphine is 5.5×10^5 L mol^{-1} s^{-1} [5]. Hence, *trans* nitroso oxide reacts under these conditions with phosphine, while nitrile oxide **1** results only from *cis* nitroso oxide. The yield of nitrile oxide **1**, equal to the yield of *cis* nitroso oxide, was 15%, the yield of Ph_3PO, equal to the yield of nitrosobenzene and *trans* nitroso oxide, was 24% to give a total of 40%, which coincides with the total yield of nitroso oxide obtained in run 2 (table). Consequently, nitrile oxide *cis* the product of transformation of both isomeric forms.

Thus, we have shown for the first time that the monomolecular reaction of consumption of the **trans** form of nitroso oxide under thermal activation conditions is isomerization into the **cis** form, which in turn undergoes rearrangement with the opening of benzene ring. The product of this rearrangement, a conjugated diene **1** with nitrile oxide and aldehyde terminal groups, was isolated and characterized by spectral methods for the first time. Nitro- and nitrosobenzenes detected upon a steady-state photooxidation of aryl azides are most likely to appear from the photolytic transformations of the nitroso oxides.

ACKNOWLEDGMENTS

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