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# Thermal Intramolecular Transformation of Key Intermediates in the Photooxidation of *para*-Allyl-Substituted Phenyl Azide

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Abstract. The electronic spectra, kinetic regularities and the mechanism of decay of the cis and trans isomeric forms of 4-[(2*E*)-1-methylbut-2-en-1-yl]phenylnitroso oxide (2) were studied by flash photolysis and product analysis. The mechanism of the consumption of this nitroso oxide is the same as the one proposed earlier for 4-methoxyphenylnitroso oxide. The *trans*-2 isomer is converted into *cis*-2, which undergoes cyclization to the substituted benzo[d][1,2,3]dioxazole **3**. The reopening of dioxazole ring yields nitrile oxide. **4**. The final product (3,4-dimethyl-3a,4-dihydro-2,1-benzisoxazol-5(3H)-ylidene)acetaldehyde (**5**) is formed by the intramolecular [3+2]-cycloaddition of the nitrile oxide group of **4** to the allylic double bond. To support the proposed mechanism, the quantum chemical calculations have been employed.

KEYWORDS: Nitroso oxides, Kinetics of decay, Flash photolysis, Mechanism, Nitrile oxides.

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#### Introduction

During the photolysis of aromatic azides in aerated solutions, the reaction of triplet nitrenes with molecular oxygen leads to reactive intermediates – nitroso oxides:<sup>1–4</sup>

$$ArN_3 \xrightarrow{hv} {}^{1}ArN \longrightarrow {}^{3}ArN \xrightarrow{O_2} {}^{2}ArNOO$$

They have been known since 1971, when the formation of the corresponding nitroso oxide was registered during 1,4-diazobenzene photolysis in aerated glassy matrices.<sup>5</sup> Since then, several groups of researchers have studied the properties these intermediates using experimental<sup>6–22</sup> and theoretical methods.<sup>8,22–26</sup> Structure and reactivity of nitroso oxides have been discussed in a number of reviews.<sup>1–4</sup>

Owing to the one-and-a-half order of the N–O bond,<sup>8,25</sup> *cis–trans* isomerism is typical for nitroso oxides:



Isomers have been detected for 4-amino-<sup>6-8</sup> and 4-nitrophenylnitroso oxides<sup>13</sup> in matrices by UV- and IR-spectroscopy. In our previous work,<sup>18</sup> the electronic spectra and kinetic regularities of decay of the isomeric forms of a number of arylnitroso oxides were studied by flash photolysis in solutions. The isomeric forms of all the studied nitroso oxides were consumed by a first-order reaction.

Until recently, there has been a lack of clarity on the mechanism of decay of nitroso oxides. The corresponding nitro- and nitrosobenzenes are always formed in small amounts during the photooxidation of aromatic azides.<sup>17,27,28</sup> They were thought to be the final products of nitroso oxide transformations. Not long ago, using 4-methoxyphenyl azide as an example, we showed that a sequence of transformations takes place during the photolysis of aromatic azides in the presence of oxygen (Scheme 1).<sup>29</sup>





According to Scheme 1, the monomolecular decay reaction of the trans form of nitroso oxides is isomerization into the cis form. The two-stage transformation of the cis form leads to the final product, a conjugated diene with nitrile oxide and aldehyde groups at the termini of the molecule. To support a two-step mechanism, the monomolecular rearrangement of cis-form of a number of arylnitroso oxides has been studied computationally.<sup>30</sup> It should be noted that these reactions of the consumption of isomeric forms of nitroso oxides (Scheme 1) are thermal.<sup>29</sup> The photochemical reaction of nitroso oxides is reported to result in the formation of the corresponding nitro compounds.<sup>9,31</sup>

Nitrile oxides are important synthetic intermediates, and are usually unstable compounds.<sup>32,33</sup> Nitrile oxide formed from 4-methoxyphenylnitroso oxide (Scheme 1,  $R = CH_3O$ ) are stable enough that we were able to accumulate it in an amount sufficient to be identified.<sup>29</sup> An intramolecular [3+2]-cycloaddition reaction is typical of nitrile oxides.<sup>34,35</sup> When the substituent R in the aromatic ring of the azide (Scheme 1) contains a double bond, for example the allylic type, the intramolecular cyclization of the nitrile oxide group to the olefinic fragment leading to the stable heterocycle will be added to the sequence of transformations. In this case, the task of accumulation and identification of the final products of the transformations of nitroso oxides is simplified and the verification of a proposed mechanism (Scheme 1) for other nitroso oxides is facilitated.

In this paper, we report on the mechanism of photooxidation of 4-[(2E)-1-methylbut-2-en-1-yl] phenyl azide (1). The kinetics of decay of the cis and trans isomers of nitroso oxide 2 were studied by flash

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photolysis in acetonitrile, benzene, and hexane. The products of the photolysis of azide **1** in the presence of oxygen were isolated and identified. The quantum chemical modeling of the elementary reaction steps were performed to determine the rate-limiting step.



#### **Experimental Section**

HPLC grade acetonitrile (Panreac) and hexane (Cryochrom) were used without further purification. Benzene was purified as described in ref. 36. Triphenylphosphine was recrystallized from ethanol.

**NMR spectra** were registered on a Bruker AM-300 MHz spectrometer in deuterated acetonitrile (Acros Organics, degree of deuteration 99.95%) using TMS as the internal standard.

UV-vis spectra were registered on a Shimadzu UV-365 spectrometer.

**HRMS analysis** was performed on a ThermoFinnigan MAT95XP mass spectrometer (EI, 70 eV, direct inlet).

**HPLC analysis** was carried out on an YL9100 liquid chromatograph equipped with a two-wave UV– vis detector. The reverse-phase analytical column was a Wakosil II 5C18 RS  $4.6 \times 250$  mm (SGE), the mobile phase was acetonitrile, the flow rate of mobile phase was 1 mL min<sup>-1</sup>, and the column was operated at room temperature. The detection wavelengths were 250 and 310 nm. A Luna 10u C18 10 × 250 mm column (Phenomenex) was used for preparative separation of the reaction mixtures.

**Kinetic Experiments.** A flash photolysis system previously described<sup>19</sup> was used for the kinetic experiments. The photolytic source was an IFP 5000-2 lamp; the maximum pulse energy was 400 J at U = 5 kV, C = 32  $\mu$ F; ~90% light energy was emitted in 50  $\mu$ s. The detector is the photomultiplier tube

with the Sb-Cs photocathode, which has a spectral response in the range of 250–650 nm. The time response is determined by the time constant of the registration channel (10  $\mu$ s). The reactor was a quartz cell with an optical path length l = 10 cm, inner diameter of ~1 cm and volume of ~8 mL. The flash photolysis of 2.5 × 10<sup>-4</sup> M azide 1 solutions saturated with oxygen was performed with filtered light (UFS-2 light filter; transmittance range,  $\lambda = 270-380$  nm).

Synthesis of 4-[(2*E*)-1-methylbut-2-en-1-yl]aniline. 4.2 g (45 mmol) of aniline, 3.2 g (47 mmol) of piperylene, 1.5 g (11 mmol) of AlCl<sub>3</sub>, and 4 mL of hexane was placed into a 17 mL rotating stainless steel autoclave. The autoclave was heated at 130°C for 4 hours, and then cooled. The reaction mixture was neutralized with a 30% NaOH solution in water. The organic layer was extracted with *tert*-buthyl-methylether and dried over KOH. The solvent was evaporated; the residue was distilled under vacuum. Amine was isolated by chromatographing the boiling fraction at 105-110°C on an alumina column and eluting with light petroleum (b.p. 40-65°C). 4-[(2*E*)-1-Methylbut-2-en-1-yl]aniline was obtained as a yellow liquid in a yield of 5.1 g (70%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm, J, Hz): 6.88 (d, 2 H, J = 7.8); 6.63 (d, 2 H, J = 7.8); 5.61 (ddd, 1 H, J = 13.0, 7.0, 1.2); 5.46 (dq, 1 H, J = 13.0, 6.3); 3.53 (s, 2 H (NH<sub>2</sub>)); 3.31 (q, 1 H, J = 7.0); 1.70 (d, 3 H, J = 6.3); 1.33 (d, 3 H, J = 7.0). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 142.5, 137.0, 136.7, 125.4, 122.9, 115.1, 41.5, 21.7, 17.9.

**4-[(2***E***)-1-Methylbut-2-en-1-yl]phenyl azide (1)** was synthesized from 4-[(2*E*)-1-methylbut-2-en-1yl]aniline via the procedure described in the literature for *trans*-1-(*o*-azidophenyl)-1-pentene.<sup>37</sup> **1** was obtained as a yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm, J, Hz): 7.20 (dd, 2 H, J = 8.5, 1.7); 6.95 (dd, 2 H, J = 8.5, 2.0); 5.40-5.62 (m, 2 H), 3.40 (q, 1 H, J = 7.0); 1.70 (d, 3 H, J = 6.1); 1.31 (d, 3 H, J = 7.0). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 143.3, 137.5, 135.8, 128.5, 123.9, 118.9, 41.7, 21.4, 17.0.

**Photooxidation of 4-[(2***E***)-1-methylbut-2-en-1-yl]phenyl azide (1).** Azide 1 (6.5 mg, 0.035 mmol) was dissolved in 35 mL of acetonirile and placed in a thermostatically controlled (20°C) quartz reactor. To saturate the solution with oxygen,  $O_2$  was bubbled through it for 5 min. The resulting solution was further purged with oxygen and irradiated by means of a xenon lamp through BS-4 and UFS-2 filters

(300–380 nm) until the starting material had disappeared. The reaction mixture was concentrated to about 0.5 mL and separated chromatographically.

(3,4-Dimethyl-3a,4-dihydro-2,1-benzisoxazol-5(3H)-vlidene)acetaldehyde (5) was isolated in an amount of 4.7 mg (70% per consumed azide). Spectral data for isomers of 5: 5a - <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) = 10.06 (d, J = 7.9 Hz, 1H, CHO), 6.72 (d, J = 9.7 Hz, 1H, H(6)), 6.57 (d, J = 9.7 Hz, 2H, 2H, 2H, 2H) Hz, 1H, H(7)), 5.96 (d, J = 7.9 Hz, 1H, H(10)), 4.52 (m, 1H, H(3)), 3.95 (m, 1H, H(4)), 3.18 (dd, J =12.6 Hz, J = 6.3 Hz, 1H, H(3a)), 1.46 (d, J = 6.3 Hz, 3H, H(8)), 1.12 (d, J = 6.9 Hz, 3H, H(9)). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN):  $\delta$ (ppm) = 192.01 (C(11)), 159.01 (C(7a)), 156.88 (C(5)), 136.35 (C(6)), 128.42 (C(7)), 123.96 (C(10)), 80.25 (C(3)), 54.42 (C(3a)), 30.40 (C(4)), 18.85 (C(8)), 16.53 (C(9)). **5b** - <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) = 10.15 (d, J = 7.7, 1H, CHO), 7.46 (d, J = 9.9 Hz, 1H, H(6)), 6.78 (d, J = 9.9 Hz, 1H, H(7)), 5.92 (d, J = 7.7 Hz, 1H, H(10)), 4.47 (m, 1H, H(3)), 3.20 (dd, J = 7.7 Hz, 1H, H(10)), 4.27 (m, 1H, H(10))), 4.27 (m, 1H, H(10)), 4.27 (m, 1H, H(10))), 4.27 (m, 1H, H(10))) 12.6 Hz, J = 6.3Hz, 1H, H(3a)), 2.97 (m, 1H, H(4)), 1.44 (d, J = 6.1 Hz, 3H, H(8)), 1.05 (d, J = 6.3 Hz, 3H, H(9)). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) = 191.90 (C(11)), 158.72 (C(7a)), 156.75 (C(5)), 128.97 (C(6)), 128.54 (C(7)), 123.75 (C(10)), 80.37 (C(3)), 54.60 (C3a)), 37.96 (C(4)), 18.72 (C(8)), 16.23 (C(9)). **5c** - <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) = 10.20 (d, J = 7.5 Hz, 1H, CHO); 7.62 (d, J = 10.0 Hz, 1H, H(6)), 6.76 (d, J = 10.0 Hz, 1H, H(7)), 5.91 (d, J = 7.5 Hz, 1H, H(10)), 4.34 (m, 1H, H(3), 2.75 (m, 1H, H(4)), 2.72 (dd, J = 12.0 Hz, J = 6.3 Hz, 1H, H(3a)), 1.52 (d, J = 6.3 Hz, 3H, H(8)), 1.20 (d, J = 6.9 Hz, 3H, H(9)). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) = 191.88 (C(11)), 158.25 (C(7a)), 156.92 (C(5)), 131.96 (C(6)), 126.66 (C(7)), 123.52 (C(10)), 84.46 (C(3)), 56.41 (C(3a)), 39.87 (C(4)), 19.97 (C(8)), 14.95 (C(9)).

**Computational Methods.** Quantum-chemical calculations were performed with the program package Gaussian 09.<sup>38</sup>

The trans isomers of nitroso oxides have a significant contribution of the diradical resonance form to the electronic structure of the molecule. So, the B3LYP and G3MP2B3 methods used successfully to study the reactions of the cis form<sup>30</sup> are not suitable for the investigation of the *trans–cis* isomerization.

The B3LYP method significantly overestimates the stability of singlet diradicals,<sup>39</sup> which leads to an underestimation of the *trans*  $\rightarrow$  *cis* isomerization energy barrier.<sup>30</sup> In the case of the composite method, G3MP2B3, one of the stages of calculations is carried out at the MP2 level, which is not applicable for diradical systems. As the cis isomers of nitroso oxides have mainly a zwitterionic nature, the transformation of the cis form of nitroso oxide **2** can be investigated at the UB3LYP/6-311+G(d,p) and G3MP2B3 levels of theory. Recently, it was shown for the non-substituted nitroso oxide HNOO that the pure functionals mPWPW91 and OLYP satisfactorily describe the *trans–cis* isomerization of nitroso oxides.<sup>30</sup>

So, in this work, all transformations were studied at the G3MP2B3, UB3LYP/6-311+G(d,p), UOLYP/6-311+G(d,p), and UmPWPW91/6-311+G(d,p) levels of theory (See Supporting Information, Table S1, S2). The latter method showed the best agreement with the experimental activation energy of the *trans–cis* isomerization and *ortho*-cyclization of the nitroso oxide **2** (Table 1). Therefore, we will discuss the energy characteristics, obtained using the UmPWPW91/6-311+G(d,p) method.

The symmetry of the systems of  $\alpha$  and  $\beta$  electrons of the initial guess wave function was not restricted by the application of these methods with the exception of G3MP2B3. The UB3LYP/6-311+G(d,p) calculation of *trans-2* accompanied by a triplet contamination of the wavefunction ( $\langle S^2 \rangle = 0.42$ , 0.03 after annihilation of the triplet component). The UmPWPW91/6-311+G(d,p) calculation of transition state **TS**(*trans-2*, *cis-2*) accompanied by the high spin contamination of the wavefunction ( $\langle S^2 \rangle = 1.02$ , 0.14 after annihilation of the high spin components; 1.02, 0.16 and 1.04, 0.31 by UOLYP/6-311+G(d,p) and UB3LYP/6-311+G(d,p), respectively).

For each compound and for each of the selected methods, the optimization of the structure and the vibrational frequency analysis were performed. The correspondence of the transition states to the reagents and products was confirmed by scanning the intrinsic reaction coordinate. Thermodynamic parameters and activation energies were calculated for T = 298.15 K.

The visualization of the results of the quantum-chemical calculations was performed with the program ChemCraft 1.6.<sup>40</sup>

#### **Results and Discussion**

#### Kinetics of Decay and Electronic Spectra of the Isomeric Forms of Nitroso Oxide 2

Transient absorption, which decays within ~20 sec, was observed upon flash photolysis of azide 1 solutions in acetonitrile, benzene, and hexane in the presence of oxygen in the wavelength region of 360–490 nm (Figure 1). In acetonitrile and benzene, the shape of the decay kinetic curves of transient absorption depends on the observation wavelength. The kinetic curves registered in the long-wavelength region ( $\lambda > 440$  nm) were described by a first-order equation (Figure 1, Curve 1):

$$A - A_{\infty} = (A_0 - A_{\infty})e^{-kt}, \qquad (1)$$

where  $A_0$  and  $A_{\infty}$  are optical densities of the solution immediately after excitation and at the end of the reaction, respectively.

The kinetic curves recorded at wavelengths from 360 to 440 nm were well-approximated by a biexponential equation (2) (Figure 1, Curve 2). This means that the observed transient absorption corresponds to the two intermediates, each of which decays by a first-order law.

$$A = A_{\infty} + A_0^I e^{-k^I t} + A_0^{II} e^{-k^{II} t}$$
(2)

where  $A_0^I$ ,  $A_0^{II}$ ,  $k^I$ ,  $k^{II}$  are the initial optical densities and rate constants of unimolecular decay of the former and latter intermediate, respectively;  $A_{\infty}$  is the final absorbance of the solution.

By equation (1) from the kinetic curves registered at the wavelengths of 450–490 nm, the rate constant were obtained, which are equal to  $k^{II}$  obtained using equation (2). Thus, we observed the consumption of the two species. The more labile of them absorbs light in the wavelength range of 360–440 nm. The absorption spectrum of second intermediate is in the 360–490 nm range.

The absorption spectra of the two species in acetonitrile and benzene were constructed from the initial optical densities calculated by equations (1) and (2) (Figure 2). The absorption maximum of the more reactive intermediate was  $\sim$ 390 nm in both solvents, and the less reactive had a maximum of  $\sim$ 425 nm in acetonitrile and  $\sim$ 420 nm in benzene. Since transient absorption is absent in the mentioned wavelength

region upon flash photolysis of deaerated solutions of azide 1, one can state that the observed species are cis and trans isomers of nitroso oxide 2.

According to theoretical calculations,<sup>8,25</sup> the cis isomers of nitroso oxides absorb light in a shorter wavelength range than the trans isomers. As a consequence, the more labile intermediate formed upon flash photolysis of azide **1** solutions in the presence of oxygen was the cis form of nitroso oxide **2**, while the more stable one was the trans form.

In hexane, the shape of the decay kinetic curves of transient absorption was independent of the observation wavelength. These kinetic curves are described well by equation (1) at all wavelengths (360–490 nm) (Figure 3, Curve 1). This indicates that in a given solvent, the two species are consumed with similar rate constants. Recently, it was shown that isomeric forms of nitroso oxides exhibit different reactivity toward organic substrates, in particular to triphenylphosphine.<sup>20</sup> Generally, the trans isomer reacts with the substrate, whereas the cis isomer is much less reactive. This feature of isomeric forms can be used for their kinetic separation in cases where the decay rate constants of the two species are similar. When flash photolysis of the azide 1 solution in hexane is performed in the presence of additives of triphenylphosphine, the two-component kinetic curves of the transient absorption decay recorded in the wavelength region of 360–430 nm are approximated well by equation (2) (Figure 3, Curve 2). The fast part of the kinetic curves corresponds to the consumption of the trans isomer of nitroso oxide 2 by the reaction with triphenylphosphine, while the slow part corresponds to the consumption of the cis isomer. We calculated the initial optical densities of the two species by equation (2) and constructed their absorption spectra in hexane (Figure 4). The absorption maxima were ~385 and ~410 nm for the cis and trans isomers, respectively.

The rate constant of the decay of the isomers of nitroso oxide **2** at 295 K in acetonirile and benzene are calculated by equations (1) and (2) and listed in Table 1. In hexane, the rate constant of the trans isomer consumption was obtained by the treatment of the kinetic curves of transient absorption decay registered at wavelengths  $\lambda > 430$  nm using equation (1) (Table 1). To determine the rate constant magnitude of the cis isomer decay in hexane, the linear dependence of the effective rate constant of its consumption *vs*. the

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concentration of Ph<sub>3</sub>P was obtained. From its intercept, the rate constant of the cis isomer decay was calculated (Table 1). The temperature dependences of isomer decay rate constants were studied in the range of 278–338 K. These dependences are described well by the Arrhenius law. Table 1 lists the magnitude of activation energy and pre-exponential factors of the decay of cis and trans isomers in acetonitrile, benzene, and hexane. The activation energy of trans isomer decay was 3-8 kJ mol<sup>-1</sup> higher than that of the cis isomer. For both species, the activation energy in hexane was 10-12 kJ mol<sup>-1</sup> lower than that in acetonitrile and benzene. The ratio cis/trans rate constant was ~2 in hexane and increased to ~8 in benzene and to ~20 in acetonitrile (Table 1).

#### Mechanism of Azide 1 Photooxidation: Product Analysis.

On the basis of the results obtained earlier for 4-methoxyphenylnitroso oxide as an example (Scheme 1)<sup>29</sup> and taking into account the ability of nitrile oxides to undergo intramolecular cycloaddition to the double bond,<sup>34,35</sup> we expected that photooxidation of azide **1** would occur in accordance with Scheme **2**. Scheme **2** 



The photolysis of the solution of azide 1 ( $1 \times 10^{-3}$  M) in acetonitrile saturated with oxygen was performed using the filtered light of a xenon lamp ( $\lambda = 300-380$  nm) at 293 K. The wavelength range of irradiation was chosen in such a way to minimize the possible photochemical reactions of nitroso oxide. The progress of the reaction was monitored by reversed-phase HPLC (See Experimental Section). Judging from the chromatogram of the reaction mixture (Figure 5), the photooxidation of azide 1 yields a single product, which was isolated and analyzed. On the basis of the <sup>1</sup>H NMR spectrum, we can conclude that the obtained compound consists of three isomeric forms, since each signal group of this spectrum contains three similar signals with an intensity ratio of ~1 : 1.7 : 2.9 (Figure 6). This is most clearly seen in the area of signals of aldehyde protons where three doublets with chemical shifts of 10.06, 10.15, and 10.20 ppm are observed. The <sup>13</sup>C NMR spectrum contains eleven signal groups, each of which consists of three signals corresponding to three isomeric forms of the same compound (Figure 7). The obtained product was identified as (3,4-dimethyl-3a,4-dihydro-2,1-benzisoxazol-5(3*H*)-ylidene)acetaldehyde **5** (Scheme 2) (See Experimental Section). Benzisoxazole **5** is formed as a mixture of three isomers **5a**, **5b**, and **5c** with a percentage ratio of 52%, 30%, and 18%, respectively (Scheme 3).

Scheme 3



The parent azide was used as a racemic mixture, so the isomerism of compound **4** is caused by cis/ trans orientation of the methyl substituent at C(4). In addition, the isomers differ by the aldehyde group position with respect to the double bond C(5)=C(10). In accordance with Scheme 2, the location of substituents must be maintained during the formation of nitrile oxide **4** from the aromatic ring. In this case, the formation of benzisoxazole **5** with the trans aldehyde group as in the isomers **5b** and **5c** should be expected. However, the conformer **5a** prevails in the mixture (52%), possibly due to *trans-cis* isomerization of the nitrile oxide **4** by keto-enol tautomerism:



The structure of compound **5** was confirmed by mass spectrometry. The mass spectrum was obtained (EI, 70eV), m/z: 191 [M]<sup>+</sup> (100%), 176 [M-CH<sub>3</sub>]<sup>+</sup> (33.9%), 165 [M-C<sub>2</sub>H<sub>2</sub>]<sup>+</sup> (4.6%), 162 [M-CHO]<sup>+</sup> (10.0%), 149 [M-CHCHO]<sup>+</sup> (20.0%), 147 [M-C<sub>2</sub>H<sub>4</sub>O]<sup>+</sup> (49.8%), 132 [M-C<sub>2</sub>H<sub>5</sub>NO] (24.6%). The mass of the molecular and fragmentation ions correspond to the proposed structure. From the high resolution mass spectrum, the molecular mass of the compound **5** was found: 191.0932. For the empirical formula C<sub>11</sub>H<sub>13</sub>NO<sub>2</sub> it is calculated: 191.0941. The absorption maximum of benzisoxazole **5** in acetotonitrile was 313 nm ( $\varepsilon = 1.55 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>).

The yield of benzisoxazole **5** was ~70% per consumed azide. Since other products were not formed in the course of the reaction under study, it can be concluded that the transformations of both isomeric forms of nitroso oxide **2** led to the same product. So, the mechanism of decay of aromatic nitroso oxides proposed recently (Scheme 1)<sup>29</sup> is valid for nitroso oxide **2**. The kinetic parameters obtained by flash photolysis (Table 1) correspond to the isomerization of the trans nitroso oxide **2** into the cis isomer and to the decay of the cis isomer via cyclization (Scheme 2). Thus, the monomolecular reactions of the consumption of cis and trans isomers of nitroso oxide **2** are of a different nature. Therefore, the polarity of the solvent has a different effect on the rate constant of the two reactions (Table 1).

#### Theoretical Investigations of the Elementary Reaction Steps.

The elementary steps of the transformation of the isomeric forms of nitroso oxide **2** into the final product were investigated by quantum-chemical methods (for the choice of methods, see the Experimental Section).

It was found that the enthalpy  $H^{\circ}$  of the cis form of nitroso oxide 2 was 6.0 kJ mol<sup>-1</sup> lower than that of the trans form (Table 2, Reaction 1). According to our preliminary calculations, the same regularity is observed for other aromatic nitroso oxides. The molecule of the cis form of nitroso oxides is stabilized by

specific interactions such as orbital overlap between the lone pair of the terminal O atom and the antibonding  $\sigma$ -ortho-C–H orbital of the aromatic ring as well as the  $n_{\sigma}(N) \rightarrow \sigma^*(O-O)$  interaction.

The transition state (TS) of the *trans*  $\rightarrow$  *cis* isomerization of nitroso oxide **2** was localized. It is characterized by the N–O-bond lengthened by 0.2 Å compared to that in the reagent and product as well as the perpendicular orientation of the O–O bond with respect to the aromatic ring plane. In the TS, the length of the O–O bond is slightly (0.01 – 0.04 Å) shorter than that in the molecules of the reagent and product. The sole imaginary frequency (210*i* cm<sup>-1</sup>) corresponds to the rotation of the N–O bond and the change in the C–N–O bond angle and, therefore, to the process of *trans–cis* isomerization.

The activation barrier ( $\Delta H^{\neq}$ ) of the trans  $\rightarrow$  cis isomerization of nitroso oxide **2** was calculated to be 69.2 kJ mol<sup>-1</sup> (Table 2, Reaction 1). This magnitude is in quite good agreement with the experimental activation energy (64.0–73.7 kJ mol<sup>-1</sup>) (Table 1).

As follows from the experimental data, in spite of the greater thermodynamic stability of the cis form of nitroso oxide **2**, this species is kinetically less stable than the trans form. This is due to the fact that the cis form decays via the ortho-cyclization reaction (Scheme 2), the activation energy of which is lower than that of *trans–cis* isomerization in all solvents (Table 1).

The transition state of the ortho-cyclization of the cis isomer of nitroso oxide **2** was localized (**TS**(*cis*-**2**, **3**)) (Figure 8). The activation barrier of this reaction was calculated to be 66.4 kJ mol<sup>-1</sup> (Table 2, Reaction 2). This magnitude agrees well with the activation energies of the decay reaction of the cis isomer of nitroso oxide **2** obtained by flash photolysis (Table 1). Reaction 2 is thermodynamically favored: the enthalpy change is -143.9 kJ mol<sup>-1</sup>.

We were unable to localize the dioxazole **3** at the UmPWPW91/6-311+G(d,p) level of theory: the ortho-cyclization of nitroso oxide **2** leads immediately to the formation of the nitrile oxide **4** (Scheme 2). But the investigations at the B3LYP/6-311+G(d,p) and G3MP2B3 levels of theory showed that the ring opening of the cycle **3** is characterized by a negligible activation barrier of 7.6 kJ mol<sup>-1</sup> (B3LYP/6-311+G(d,p)) and 18.3 kJ mol<sup>-1</sup> (G3MP2B3) (See Supporting Information, Table S2).

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The transition states of the intramolecular [3+2]-cyclization of nitrile oxide 4 resulted in the formation of the isomers of benzisoxazole **5b** and **5c** (Schemes 2 and 3): **TS(4, 5b)** and **TS(4, 5c)** (Figure 8). The activation barriers of these reactions were calculated as  $35.0 \text{ kJ} \text{ mo}\Gamma^1$  (Table 2, Reaction 3) and  $38.8 \text{ kJ} \text{ mo}\Gamma^1$  (Table 2, Reaction 4). Reactions 3 and 4 are thermodynamically favored: the calculated enthalpy change values are -149.1 and -149.2 kJ mo $\Gamma^1$ , respectively.

As can be seen from Table 2, the activation barrier of the intramolecular [3+2]-cycloaddition of nitrile oxide 4 to the double bond is lower than that of ortho-cyclization of the cis form of nitroso oxide 2 (66.4 kJ mol<sup>-1</sup>), i.e. the process of reaction product formation is limited by this step. The trans form of nitroso oxide 2, ultimately, also transforms into product 5 and, in this case, the slowest step is *trans*-2  $\rightarrow$  *cis*-2 isomerization, as evidenced by the experimental results (Table 1). We cannot exclude the fact that this isomerization may be reversible. If the reverse reaction takes place, it would influence the kinetic regularities of the decay of trans isomer of nitroso oxide 2; however, this was not observed (Figure 1, the kinetic curve registered at 480 nm). Consequently, the *cis*-2  $\rightarrow$  *trans*-2 conversion loses in competition with the ortho-cyclization of *cis*-2.

#### Conclusion

On the basis of the obtained results, we can conclude that the mechanism of the decay of the isomeric forms of nitroso oxide 2 is the same as that proposed earlier for 4-methoxyphenylnitroso oxide. The consumption rate constant of the trans isomer of nitroso oxide 2 measured by flash photolysis is the rate constant of its isomerization into the cis isomer. The consumption rate constant of the cyclization to dioxazole cycle. The activation energy magnitude of the conversion of the trans isomer of nitroso oxide is in the range of 64.0-73.7 kJ mol<sup>-1</sup>, depending on the nature of the solvent. The activation energy of the consumption reaction of the cis isomer is 56-68.2 kJ mol<sup>-1</sup>. The isomerization of the cis form into the trans form has no appreciable effect on the observed kinetic regularities of the decay of nitroso oxide 2. This means that the energy cost required for this reaction is much greater than that required for the cyclyzation of *cis*-2. The final product of the

transformations of both isomeric forms of nitroso oxide 2 is benzisoxazole 5. The nature of the ratelimiting step of the process depends on the transformation of the species considered. If product 5 is formed from the trans form of nitroso oxide, then the rate-limiting step is the isomerization *trans*-2  $\rightarrow$ *cis*-2. In the case where the final product is formed from the cis form, the process is limited by the step of its cyclization.

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**Supporting Information Available:** NMR spectra of the mixture of the isomers **5a**, **5b**, and **5c**. Total energies and thermodynamic parameters of compounds and transitions states calculated by quantum-chemical methods. Thermodynamic and activation parameters of elementary steps of transformation of nitroso oxide **2** into the final product **5** calculated by quantum-chemical methods and Cartesian coordinates. This material is available free of charge via the Internet at <a href="http://pubs.acs.org">http://pubs.acs.org</a>.

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Table 1. Rate Constants (T = 295 K) and Activation Parameters of Decay of Isomeric Forms of troso Oxide 2.

solvent	cis			trans			
Solvent	$k_{ m cis}({ m s}^{-1})$	$\log k^{0}_{\rm cis}$	$E_a (kJ mol^{-1})$	$k_{\text{trans}} (s^{-1})$	$\log k^{\theta}_{\text{trans}}$	$E_a (kJ mol^{-1})$	
C <sub>6</sub> H <sub>14</sub>	$0.52 \pm 0.02$	9.7 ± 0.5	56 ± 3	$0.25 \pm 0.04$	$10.6 \pm 0.2$	$64 \pm 1$	
$C_6H_6$	$1.45\pm0.09$	$11.3 \pm 0.1$	$68.2\pm0.7$	$0.172\pm0.006$	$12.8\pm0.2$	$71.4\pm0.9$	
CH <sub>3</sub> CN	$2.75\pm0.08$	$12.0 \pm 0.2$	$66 \pm 2$	$0.133\pm0.002$	$12.0 \pm 0.1$	$73.7\pm0.7$	

ble 2. Thermodynamic and Activation Parameters of Elementary Steps of Transformation of Nitroso kide 2 into the Final Product 5 Calculated by UmPWPW91/6-311+G(d,p) Method;  $\Delta S$  (J mol<sup>-1</sup> K<sup>-1</sup>), H,  $\Delta G$  (kJ mol<sup>-1</sup>).

no	reaction	$\Delta S^{\circ}$	ΔH°	ΔG°	$\Delta S^{\neq}$	$\Delta H^{\neq}$	ΔG <sup>≠</sup>
1	<i>trans</i> -2 $\rightarrow$ [TS] $\rightarrow$ <i>cis</i> -2	2.2	-6.0	-6.6	0.2	69.2	69.2
2	$\textit{cis-2} \rightarrow [\text{TS}] \rightarrow [3] \rightarrow 4$	44.0	-143.9	-157.0	-22.0	66.4	73.0
3	$4 \rightarrow [TS] \rightarrow 5b$	-77.0	-149.1	-126.1	-47.2	35.0	49.1
4	$4 \rightarrow [TS] \rightarrow 5c$	-78.0	-149.2	-125.9	-51.5	38.8	54.2

#### **Figure captions**

Figure 1. Kinetic curves of absorbance decay of nitroso oxide 2 in acetonitrile solution registered at wavelengths of 480 nm and 400 nm (T = 295 K). Solid lines correspond to the theoretical description.

Figure 2. Electronic absorption decay associated spectra of the cis and trans forms of nitroso oxide 2 in acetonitrile. T = 295 K.

Figure 3. Kinetic curves of absorbance decay of nitroso oxide 2 in hexane solution registered at wavelength of 390 nm (T = 295 K). (1) – in the absence of Ph<sub>3</sub>P; (2) – in the presence of Ph<sub>3</sub>P ( $1.2 \times 10^{-5}$  M). Solid lines correspond to theoretical description.

Figure 4. Electronic absorption decay associated spectra of the cis and trans forms of nitroso oxide 2 in hexane obtained in the presence of Ph<sub>3</sub>P ( $1.2 \times 10^{-5}$  M). T = 295 K.

Figure 5. Chromatogram of the reaction mixture obtained by photolysis of an O<sub>2</sub>-saturated acetonitrile solution of azide 1 ( $1 \times 10^{-3}$  M). The mobile phase is acetonitrile, and the detection wavelengths were 250 and 310 nm. t<sub>R</sub> = 3.12 min (product), t<sub>R</sub> = 4.78 min (azide 1).

**Figure 6.** <sup>1</sup>H NMR spectrum of the product of azide **1** photooxidation in CD<sub>3</sub>CN. TMS was used as the internal standard.

**Figure 7.** <sup>13</sup>C NMR spectra of the product of azide **1** photooxidation in CD<sub>3</sub>CN. TMS was used as the internal standard.

**Figure 8.** Optimized structures corresponding to the stationary points on the potential energy surface calculated using UmPWPW91/6-311+G(d,p).

## Figures



Figure 1.



Figure 2.



Figure 3.



Figure 4.











Figure 8.

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