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Reactions of Arylnitroso Oxides with Substituted Styrenes: Kinetics and Products

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Abstract—The kinetics of the reactions of phenylnitroso oxide and 4-CH_3O- and 4-Cl-phenylnitroso oxides with a series of substituted styrenes (4-X–C_6H_4–CH=CH_2; X = H, CH_3O, Cl, CN) in acetonitrile at 22 ± 2°C was studied using the flash photolysis technique. It was shown for 4-CH_3O–C_6H_4NOO as an example that only the *trans* isomers of the nitroso oxides are involved in the reaction. There is a linear correlation between the logarithm of the rate constant and the electronic properties of the substituent in the nitroso oxide aromatic ring on the Hammett scale: $\rho = 2.3 \pm 0.3$ ($r = 0.993$) for 4-CH_3O-styrene $\rho = 2.03 \pm 0.07$ ($r = 0.995$) for styrene, and $\rho = 1.77 \pm 0.05$ ($r = 0.9996$) for 4-Cl-styrene. Both the electron-donating and electron-withdrawing substituents in the aromatic ring of styrene increase its reactivity toward a given nitroso oxide. An analysis of the products of phenyl azide photooxidation in the presence of styrene showed that the product of phenylnitroso oxide [3+2]cycloaddition to the double bond of the olefin decomposes into benzalaniline and carbonyl oxide.

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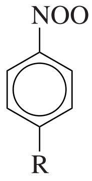
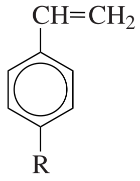
INTRODUCTION

The interaction of triplet aromatic nitrenes with oxygen yields nitroso oxides (ArNOO) [1]. The molecular structure of nitroso oxides allows *cis–trans* isomerism. The isomers differ both in spectral properties and in reactivity. This made it possible to identify them in low-temperature matrices [2–4] and, using the flash photolysis technique, in solutions near and above room temperature [5, 6]. In the ground state, the isomers are singlet species. They are 1,3-dipoles capable of [3+2]cycloaddition to dipolarophiles, such as olefins [7].

In the present work, we used flash photolysis to study the kinetics of the reactions of nitroso oxides **Ia**–**Ic** with substituted styrenes **IIa**–**IId** in acetonitrile at 22 ± 2°C and identified the products of the reaction between nitroso oxide **Ia** and olefin **IIa** in acetonitrile, benzene, and hexane.



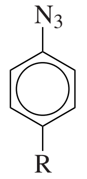
Ia: R = H
Ib: R = CH_3O
Ic: R = Cl



IIa: R = H
IIb: R = CH_3O
IIc: R = Cl
IId: R = CN

EXPERIMENTAL

Acetonitrile, benzene, and hexane were purified according to standard procedures [8]. Substituted styrenes (Lancaster) stabilized by 4-*tert*-butylcatechol were distilled under a reduced pressure. The arylnitroso oxides to be examined were generated by the flash photolysis of azides **IIIa**–**IIIc** in the presence of air. Azide **IIIa** was synthesized as described in [9]; azides **IIIb** and **IIIc**, as described in [10]. **IIIa** was distilled in vacuo, **IIIb** was recrystallized from hexane, and **IIIc** was recrystallized from ethanol.



IIIa: R = H
IIIb: R = CH_3O
IIIc: R = Cl

Kinetic studies were carried out using a flash photolysis setup, whose parameters are reported elsewhere [11]. The photolytic light source was an IFP 5000-2 lamp. The maximum energy of a pulse was 400 J at U = 5 kV and C = 32 μF, and ~90% of the light energy was emitted within 50 μs. The spectrophotometric part of the setup consisted of a probing source of continuous radiation (DKSSh-150 xenon lamp) with a system of quartz lenses and diaphragms for probing beam formation, an MDR-4 monochromator, an FEU-97 photoelectron multiplier, and an S9-8 memory oscilloscope. This setup was equipped with a computer-based pulse processing device. After the compensation of its permanent component, the signal from the photoelectron multiplier was amplified and was entered into the digital oscilloscope operating in the standby mode. The digitized signal was inputted into the computer through the KOP interface (IEEE-488, GPIB). Kinetic profiles were processed using nonlinear regression analysis. The rate constant determination error was at most 10%. The reactor was a temperature-controlled quartz cell with a length of $l = 10$ cm and an inner diameter of ~1 cm.

The flash photolysis of acetonitrile solutions of aryl azides saturated with air oxygen was performed with filtered light (UFS-2 optical filter, 270–380 nm bandpass). The initial aryl azide concentration was 2.5×10^{-4} mol/l. The styrene concentration was varied between 1×10^{-3} and 5.5×10^{-3} mol/l.

The products of the reaction between nitroso oxide **Ia** and styrene were studied under conditions of steady-state azide **IIIa** photolysis in the presence of styrene and oxygen. A solution (5 ml) of **IIIa** (9.1×10^{-3} mol/l) and **IIa** (8.7×10^{-3} mol/l) in acetonitrile, benzene, or hexane was placed in a temperature-controlled cylindrical quartz reactor. Photolysis was carried out with $\lambda = 270$–380 nm light (UFS-2 optical filter, DRT-400 mercury lamp) at 20°C under continuous oxygen bubbling. The distance between the reactor and the source of light was ~15 cm. The reaction time was 90 min. The products were analyzed by high-performance liquid chromatography (HPLC) and chromatography coupled with mass spectrometry. HPLC analyses were performed on an LC-20 liquid chromatograph (Shimadzu) equipped with an SPD-M20A UV diode array detector (Shimadzu). A Zorbax Sil column was used. The mobile phase was a hexane–isopropyl alcohol (80 : 20 vol/vol) mixture, and the flow rate of the mobile phase was 1 ml/min. The column operated at room temperature. UV detection was performed at wavelengths of 254 and 280 nm. Mass spectra were recorded using an AT 6890/AT 5973 gas chromatograph/mass-selective detector system (Agilent Technologies). The data processing system had a library consisting of 250000 spectra. The chromatographic regime was as follows: Ultra-2 column (50 m × 0.2 mm), 95% methyl silicone + 5% phenyl methyl silicone as the grafted phase, initial temperature of 40°C, a 3 min-long isotherm, final temperature of 250°C, and a heating rate of 10 K/min.

RESULTS AND DISCUSSION

Kinetics of the Reactions of Arylnitroso Oxides with Substituted Styrenes

The flash photolysis of solutions of the aryl azides in the presence of oxygen yields the *cis* and *trans* isomers of nitroso oxides, which are consumed according to the first-order rate law [6]. The introduction of olefins **IIa**–**IId** into the system increases the disappearance rate of the *trans* isomer of nitroso oxide **Ib**, whereas the disappearance rate of the *cis* isomer remains almost unchanged. The kinetics of the decrease in the absorbance of **Ib** is described by the five-parameter two-exponential equation

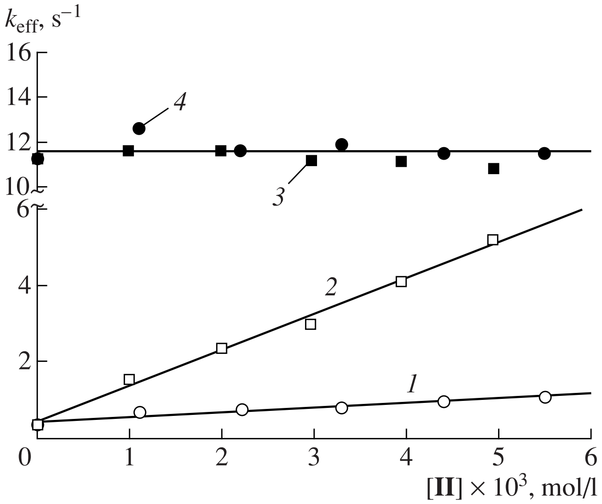


Fig. 1. Effective rate constants of disappearance of the nitroso oxide **Ib** isomers in acetonitrile at 22 ± 2°C versus the olefin concentration: (*1*) *trans* isomer + **IIa**, (*2*) *trans* isomer + **IId**, (*3*) *cis* isomer + **IIa**, and (*4*) *cis* isomer + **IId**.

$$A = A_\infty + A_0^{\text{I}} e^{-k_{\text{eff}}^{\text{I}} t} + A_0^{\text{II}} e^{-k_{\text{eff}}^{\text{II}} t}, \quad (1)$$

where A_0^{I} and A_0^{II} are the initial absorbances of the *cis* and *trans* isomers, $k_{\text{eff}}^{\text{I}}$, $k_{\text{eff}}^{\text{II}}$ are the effective rate constants of the disappearance of the *cis* and *trans* isomers, and A_∞ is the final absorbance due to the reaction products.

The effective rate constants of the disappearance of the *cis* isomer of **Ib** remain unchanged, and those of the *trans* isomer increase with an increasing concentration of the substituted styrenes (Fig. 1). The absolute rate constants for the reactions of the *trans* isomer of **Ib** with olefins **IIa**–**IId** (k_{styr}) are given in the table.

Rate constants of the reactions of the *trans* isomers of arylnitroso oxides with substituted styrenes ($k_{\text{styr}} \times 10^{-2}$, l mol^{-1} s^{-1}) in acetonitrile at 22 ± 2°C*

4-R-$C_6H_4CH=CH_2$ / 4-R-C_6H_4NOO	R = CH_3O (**IIb**)	R = H (**IIa**)	R = Cl (**IIc**)	R = CN (**IId**)
R = CH_3O (**Ib**)	1.44	1.1	1.43	9.1
R = H (**Ia**)	8.0	2.6**	4.5	6.4
R = Cl (**Ic**)	20.4	8.8	10.8	13.1

* The rate constant determination error does not exceed 10%.

** From [12].

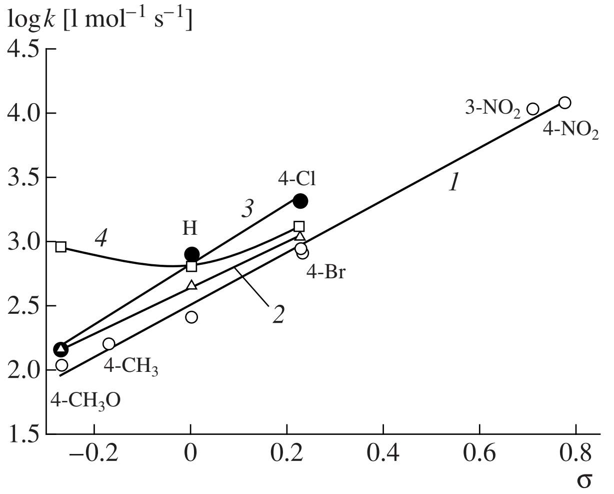


Fig. 2. Rate constants of the reactions of nitroso oxides (XC_6H_4NOO) with substituted styrenes in acetonitrile versus the electronic properties of the substituent X in terms of the Hammett equation for (*1*) **IIb**, (*2*) **IIa**, (*3*) **IIc**, and (*4*) **IId**.

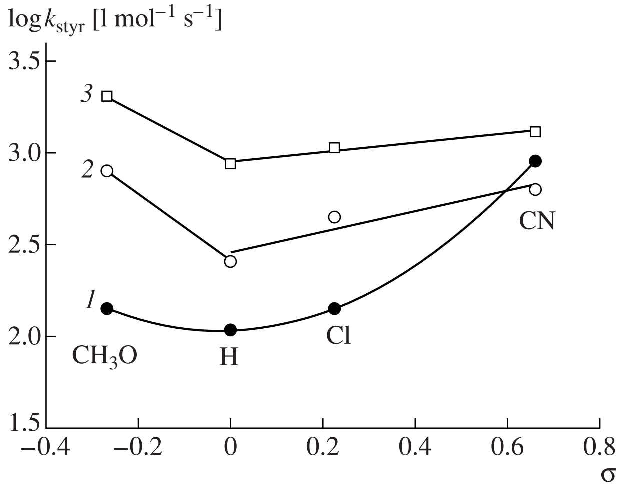


Fig. 3. Rate constants of the reactions of nitroso oxides (*1*) **Ib**, (*2*) **Ia**, and (*3*) **Ic** with substituted styrenes (4-X–$C_6H_5CH{=}CH_2$) in acetonitrile versus the electronic properties of the substituent X on Hammett's scale.

The rate constants of the monomolecular decay of the *cis* and *trans* isomers of **Ia** in acetonitrile at 22 ± 2°C are $k_{cis} = 1.19\ \text{s}^{-1}$ and $k_{trans} = 0.10\ \text{s}^{-1}$. For **Ic**, $k_{cis} = 1.77\ \text{s}^{-1}$ and $k_{trans} = 0.15\ \text{s}^{-1}$. The kinetic curves of the disappearance of these nitroso oxides, which were recorded in the wavelength range in which both isomers absorb light, cannot be fitted satisfactorily to Eq. (1) in the presence of the substituted styrenes. This can be explained as follows. If only the *trans* isomer reacts with the olefin, as in the case of **Ib**, then raising the substrate concentration will not change the disappearance rate constant of the *cis* isomer, but the effective rate constant of the disappearance of the *trans* isomer will increase. As a result, the isomers will disappear at comparable rates and will be kinetically similar. This is not the case with **Ib** because of the rather large difference between the disappearance rate constants of its isomers ($k_{cis} = 11.3\ \text{s}^{-1}$, $k_{trans} = 0.37\ \text{s}^{-1}$) and because the *trans* form of this nitroso oxide is less reactive toward the olefins examined than the *trans* isomers of nitroso oxides **Ia** and **Ic** (see the table).

In subsequent experiments, we monitored only the *trans* isomers of **Ia** and **Ic** at $\lambda = 430$ nm. The observed disappearance kinetics can be fitted well to the first-order equation

$$A - A_\infty = (A_0 - A_\infty)\exp(-k_{\text{eff}}^{\text{II}}t). \qquad (2)$$

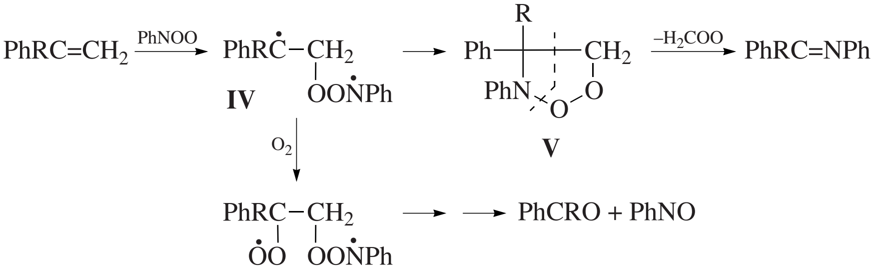
The rate constants of the reactions of the *trans* isomers of **Ia** and **Ic** with styrenes **IIa**–**IId** were derived from the slopes of the linear plots of $k_{\text{eff}}^{\text{II}}$ versus the concentration of the substrate added (table).

Earlier, we studied the reactivity of the arylnitroso oxides toward olefins with different structures [12]. We found that the electron-withdrawing substituents in the aromatic ring of the nitroso oxides increase the reaction rate constants; i.e., these species show electrophilic properties. A linear dependence of $\log k_{\text{styr}}$ on Hammett's σ constant [13] of the substituent in the nitroso oxide molecule is observed in the styrene series examined, except for **IId** (Fig. 2). The Hammett dependence for unsubstituted styrene [12] is supplemented here by the rate constants for nitroso oxides **Ib** and **Ic** (Fig. 2). The slope ratios of the straight lines have the following values: $\rho = 2.3 \pm 0.3$ ($r = 0.993$) for **IIb**, $\rho = 2.03 \pm 0.07$ ($r = 0.995$) for **IIa**, and $\rho = 1.77 \pm 0.05$ ($r = 0.9996$) for **IIc**. In this series, ρ tends to decrease with an increasing electron-withdrawing power of the substituent. In the case of **IId**, the Hammett curve is *V*-shaped, with the minimum falling on unsubstituted phenylnitroso oxide (table, Fig. 2), indicating that the rate-determining step of the reaction changes on passing from phenylnitroso oxide with the electron-donating substituent to phenylnitroso oxide with the electron-withdrawing substituent.

Consideration of the rate constant values for a given nitroso oxide as a function of the electronic properties of the substituent in the styrene molecule shows that both electron-withdrawing and electron-donating substituents increase the reactivity of olefin (table, Fig. 3). Here we will draw an analogy to reactions of carbonyl oxides, which are structurally similar to nitroso oxides. Such dependences of the reactivity of the substrate being oxidized on its structure were observed earlier for the reactions of benzophenone oxide [14] and propionaldehyde oxide [15] with some aromatic aldehydes and for the reactions of benzophenone oxide with phenols [16]. This is explained by the ambiphilic nature of the carbonyl oxides (in our case, nitroso oxides), which can show the properties of either an electrophile or a nucleophile, depending on the structure of the coreactant.

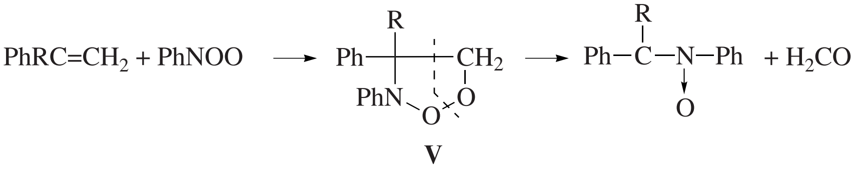
Products of the Reaction between Phenylnitroso Oxide and Styrene

The products of the reactions of phenylnitroso oxide with styrene and α-methylstyrene in acetonitrile at 20°C were identified earlier [17]. It was found that nitrobenzene, benzaldehyde (or acetophenone), and the corresponding imine are the major products of these reactions. Based on these results, the following reaction mechanism was suggested:



Scheme 1.

Ishikawa et al. [17] failed to prove that carbonyl oxide is an intermediate in this reaction. It was assumed that cyclic peroxide **V** forms by the intramolecular recombination of biradical **IV** or via the one-step mechanism. Since nitroso oxides in their ground singlet state are classical 1,3-dipoles, which can participate in [3+2]cycloaddition reactions [7], the second assumption is more likely. Note that cycle **V** can break via two pathways. One pathway is shown in Scheme 1, and the other is the formation of the corresponding nitrone and formaldehyde:



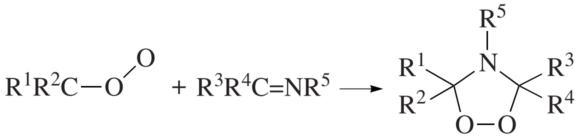
Scheme 2.

In our opinion, the decomposition of cyclic intermediate **V** into two stable molecules is more probable than its decomposition into an imine and an unstable carbonyl oxide. To check this assumption, we studied the products of phenyl azide photooxidation in the presence of styrene.

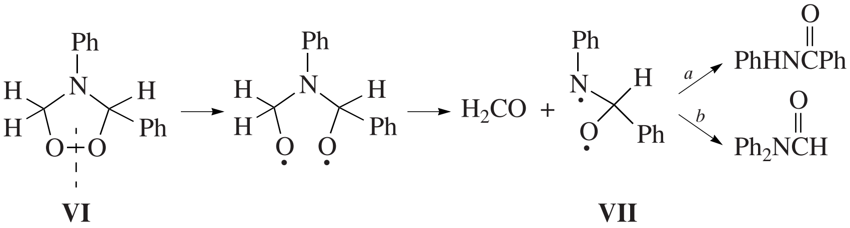
The steady-state photolysis of PhN_3 in acetonitrile was carried out in such a way that the photolytic reactions of the resulting nitroso oxide were ruled out and the PhNOO conversion products were the same as the products obtained under the thermal activation conditions (see Experimental). The reaction mixture was analyzed using HPLC. Because we failed to adjust the chromatographic conditions in order to separate the starting phenyl azide and styrene, we could only estimate approximately the extent of the reaction as the decrease in the area of the chromatographic peak corresponding to both reactants. According to this estimate, the extent of the reaction was ~30%. Identification against authentic samples showed that the products contain benzalaniline PhCH=NPh ($\sim 6 \times 10^{-4}$ mol/l, retention time of 3.453 min), nitrosobenzene ($\sim 1 \times 10^{-4}$ mol/l, 3.615 min), and nitrobenzene ($\sim 1 \times 10^{-4}$ mol/l, 4.143 min). Some peaks in the chromatogram of the reaction mixture were not assigned. Contrary to our expectations, no N,α-diphenylnitrone (retention time 7.945 min) was detected.

In order to identify the other components of the mixture, we analyzed the reaction products by chromatography coupled with mass spectrometry. The recorded mass spectra were interpreted using the HPChem Station program supplied with the chromatograph–mass spectrometer–computer system. The goodness of fit between the observed and library spectra was 93 or better. All nine parameters that determined the search strategy in the spectrum took the best values for the following compounds: azobenzene (26.8%) (EIMS, 70 eV; m/z (I_{rel}, %)): 182 [M$^+$] (26), 153 $[M–N_2H]^+$ (4), 152 $[M–N_2H_2]^+$ (11), 105 $[M–C_6H_5]^+$ (17), 77 $[C_6H_5]^+$ (100), 63 (4), 51 (33), 39 (4)), aniline (7.6%) (93 $[M]^+$ (100), 92 $[M–H]^+$ (10), 78 $[M–NH]^+$ (1), 66 $[M–CNH]^+$ (39), 65 $[M–CNH_2]^+$ (20), 39 (12)) (triplet nitrene conversionproducts), nitrobenzene (4.0%) (123 $[M]^+$ (48) 107 $[M–O]^+$ (0.5), 93 $[M–NO]^+$ (8), 77 $[M–NO_2]^+$ (100), 65 (12), 51 (42), 39 (8)), benzalaniline (36.7%) (181 $[M]^+$ (88), 180 $[M–H]^+$ (100) 152 $[M–CH_2N]^+$ (4), 104 $[M–C_6H_5]^+$ (8), 89 (4), 78 (8), 88 $[C_6H_5]^+$ (33), 51 (10)), *N*-phenylbenzamide PhNHC(O)Ph (11.2%) (197 $[M]^+$ (35), 105 $[M–C_6H_5NH]^+$ (100), 77 $[C_6H_5]^+$ (46), 51 (14), 39 (4)), and *N*,*N*-diphenylformamide $Ph_2NC(O)H$ (3.4%) (197 $[M]^+$ (100), 168 $[M–CO]^+$ (57), 168 (45), 167 (30), 104 $[M–C_6H_5NH_2]^+$ (16), 94 (12), 83 (7), $[C_6H_5]^+$ (15), 66 (20), 51 (13), 39 (4)).

Carbonyl oxides can undergo [3+2]cycloaddition with imines to form 1,2,4-dioxazolidines [18]:



It is quite probable that, if a carbonyl oxide forms as an intermediate species in the reaction under study, it will react with the imine in the solvent cage to yield 1,2,4-dioxazolidine. Dioxazolidines are thermally stable below 100°C. On heating above this temperature, they decompose with O–O bond cleavage to form biradical **VII**. The migration of the H atom in **VII** produces *N*-phenylbenzamide (route *a* in Scheme 3) [15].



Scheme 3.

Dioxazolidine **VI** formed under the reaction conditions can decompose photolytically. This can also take place in a chromatographic/mass spectrometric analysis upon sample heating in the injector of the chromatograph. As a result, the products include *N*-phenylbenzamide and *N*,*N*-diphenylformamide; the latter can result from the migration of the phenyl group to the nitrogen atom in biradical **VII** (route *b* in Scheme 3).

Only part of the resulting carbonyl oxide is consumed in the reaction with imine. Otherwise, no benzalaniline would be observed in the reaction products. The "destiny" of the carbonyl oxide that escapes from the solvent is still unclear.

The product yields for the reaction between phenylnitroso oxide and styrene in terms of consumed phenyl azide can be estimated approximately, taking into account that the conversion of phenyl azide was ~30% (~2.7×10^{-3} mol/l). If the results of both analytical methods and the imine consumed in the reaction with carbonyl oxide are taken into consideration, it will be clear that the amount of the resulting imine formed and, hence, the amount of carbonyl oxide are ~8.4×10^{-4} mol/l, which is equivalent to ~30% yield in terms of consumed azide. It is likely that nitrobenzene and nitrosobenzene are products of the conversion of the *cis* isomer of the nitroso oxide. As was mentioned above, this *cis* isomer is almost unreactive toward olefins.

We assumed that the decomposition of cyclic compound **V** into imine and carbonyl oxide is thermodynamically favorable because the carbonyl oxide is stabilized by forming a complex with acetonitrile [19]. A similar analysis of products was carried out for the reaction in nonpolar solvents (benzene and hexane). Benzalaniline was found in the reaction mixture by HPLC, and no N,α-diphenylnitron was detected again.

Thus, the composition of the products of the steady-state photolysis of phenyl azide in the presence of oxygen and styrene completely confirms the earlier finding that the reaction of arylnitroso oxides with styrene takes place through the formation of a cyclic intermediate via the [3+2]cycloaddition mechanism followed by the decomposition of this intermediate into benzalaniline and carbonyl oxide [17].

ACKNOWLEDGMENTS

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REFERENCES

1. Gritsan, N.P. and Pritchina, E.A., *Usp. Khim.*, 1992, vol. 61, no. 5, p. 910.
2. Pritchina, E.A. and Gritsan, N.P., *J. Photochem. Photobiol., A*, 1988, vol. 43, p. 165.
3. Pritchina, E.A., Gritsan N.P., and Bally, T., *Phys. Chem. Chem. Phys.*, 2006, no. 8, p. 719.

4. Inui, H., Irisawa, M., and Oishi, S., *Chem. Lett.*, 2005, vol. 34, no. 4, p. 478.
5. Chainikova, E.M., Khursan, S.L., and Safiullin, R.L., *Dokl. Akad. Nauk*, 2005, vol. 403, no. 3, p. 358 [*Dokl. Phys. Chem.* (Engl. Transl.), vol. 403, part 1, p. 133].
6. Chainikova, E.M., Khursan, S.L., and Safiullin, R.L., *Kinet. Katal.*, 2006, vol. 47, no. 4, p. 566 [*Kinet. Catal.* (Engl. Transl.), vol. 47, no. 4, p. 549].
7. Perez, P., Domingo, L.R., Aurell, M.J., and Contreras, R., *Tetrahedron*, 2003, vol. 59, p. 3117.
8. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., *Technics of Organic Chemistry*, vol. 7: *Organic Solvents: Physical Properties and Methods of Purification*, New York: Wiley, 1955.
9. Smith, P.A.S. and Boyer, J.H., *Org. Synth.*, 1963, vol. 4, p. 75.
10. Lindsay, R.O. and Allen, G.F., *Org. Synth.*, 1955, vol. 3, p. 710.
11. Maslennikov, S.I., Nikolaev, A.I., and Komissarov, V.D., *Kinet. Katal.*, 1979, vol. 20, p. 326.
12. Chainikova, E.M., Khursan, S.L., and Safiullin, R.L., *Kinet. Katal.*, 2004, vol. 45, no. 6, p. 842 [*Kinet. Catal.* (Engl. Transl.), vol. 45, no. 6, p. 794].
13. Gordon, J.G. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.
14. Murray, R.W. and Morgan, M.M., *J. Org. Chem.*, 1991, vol. 56, no. 2, p. 684.
15. Murray, R.W. and Morgan, M.M., *J. Org. Chem.*, 1991, vol. 56, no. 21, p. 6123.
16. Nazarov, A.M., Khursan, S.L., Chainikova, E.M., and Komissarov, V.D., *Kinet. Katal.*, 2001, vol. 42, no. 1, p. 42 [*Kinet. Catal.* (Engl. Transl.), vol. 42, no. 1, p. 35].
17. Ishikawa, S., Tsuji, S., and Sawaki, Y., *J. Am. Chem. Soc.*, 1991, vol. 113, no. 11, p. 4282.
18. McCullough, K.J., Mori, M., Tabuchi, T., Yamakoshi, H., Kusabayashi, S., and Nojima, M., *J. Chem. Soc., Perkin Trans. 1*, 1995, p. 41.
19. Khursan, S.L., Nazarov, A.M., Chainikova, E.M., and Komissarov, V.D., *Izv. Akad. Nauk, Ser. Khim.*, 2001, no. 5, p. 759.