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Amination of 3,5-Dibromo-4-nitrosoanilines and 3-Halo-4-nitrosophenols

E. A. Bocharova[a], L. M. Gornostaev[a], N. P. Gritsan[b], and T. N. Gurova[a]

[a]*Astaf'ev Krasnoyarsk State Pedagogical University, Krasnoyarsk, 660049 Russia*
e-mail: gornostaev@kspu.ru
[b]*Institute of Chemical Kinetics and Burning, Siberian Division, Russian Academy of Sciences, Novosibirsk, Russia*

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Abstract—Reactions of 3,5-dibromo-4-nitrosoanilines with arylamines and 3-halo-4-nitroso-phenols with alkyl- and arylamines result in the nucleophilic substitution of the halogen atoms.

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We showed formerly [1] that in reactions of 2,6-dihalonitrosoarenes with secondary amines the nitroso group remained intact but a halogen and (or) hydrogen atom in the para-position to the nitroso group suffered a nucleophilic substitution with an amino group.

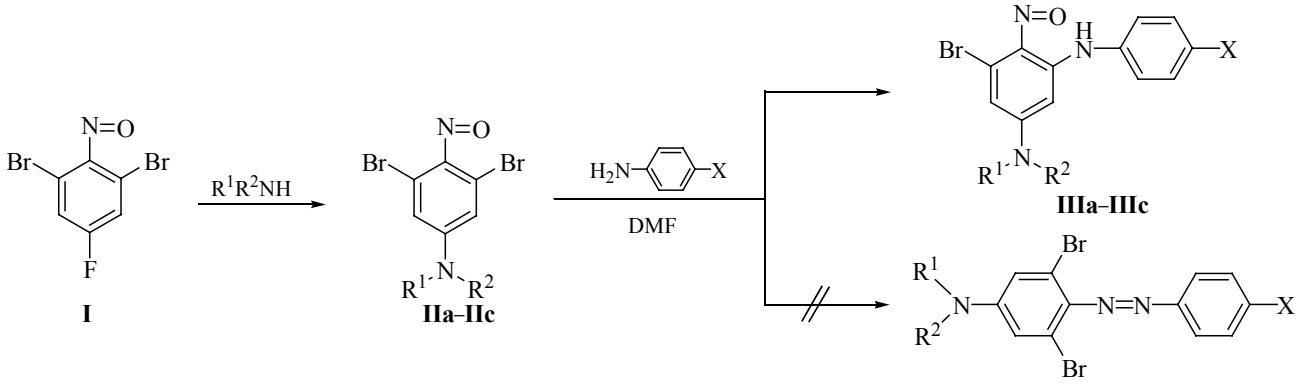
In this connection it seemed purposeful to study the reactions with various amines of aromatic *C*-nitroso compounds containing in the aromatic ring alongside the nitroso group also amino, hydroxy groups and halogen atoms. The nucleophilic substitution of halogens would provide a possibility to synthesize compounds inavailable in another way.

In this study we investigated the reactions of 3,5-dibromo-4-nitrosoanilines with primary aromatic amines, and also the amination of 3-halo-4-nitrosophenols.

The initial 3,5-dibromo-4-nitrosoanilines **IIa–IIc** prepared from 1,3-dibromo-2-nitroso-5-fluorobenzene (**I**) by procedure [1] were brought into the reaction with arylamines leading to the nucleophilic substitution of one of the bromine atoms. We obtained by this reaction previously unknown 2-nitroso derivatives of the substituted diphenylamine **IIIa–IIIc**. The alternative way involving the condensation with the formation of azo compounds did not occur (Scheme 1).

In general compounds **II** proved to be less active than compound **I**. Also by an example of the reaction of compound **I** with morpholine and *p*-toluidine the higher reactivity of morpholine in fluorine substitution was established that was also confirmed by kinetic data: the rate constant of reaction with morpholine equaled

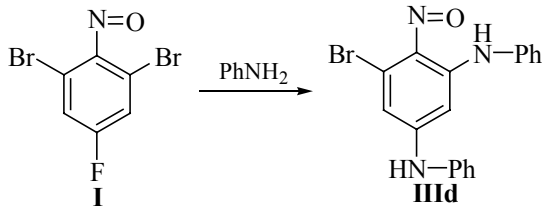
Scheme 1.



II, R^1,R^2 = $(CH_2CH_2)_2O$ (**a**); R^1 = R^2 = Me (**b**); R^1 = H, R^2 = C_6H_4=4-Me (**c**); **III,** R^1,R^2 = $(CH_2CH_2)_2O$, X = H (**a**), Me (**b**); R^1 = R^2 = Me, X = H (**c**).

11.5 l mol^{-1}s^{-1}, and with *p*-toluidine, 0.0175 mol^{-1}s^{-1}.

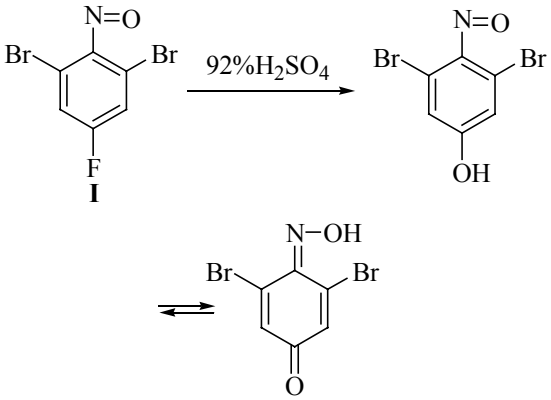
1,3-Dibromo2-nitroso-5-fluorobenzene (**I**) under the treatment with excess aniline at 50–60°C suffered nucleophilic substitution of both fluorine and bromine atoms.



I **IIId**

This reaction path followed by 1,3-dibromo-2-nitroso-5-fluorobenzene (**I**) and 3,5-dibromo-4-nitroso-anilines **II** with amines stimulated the interest in the study of the amination of 3-halo-4-nitrosophenols.

Nitrosophenols **IVa–IVc** were obtained by nitrosation of the corresponding halophenols with nitrosylsulfuric acid in the acetic acid medium [3], 2,6-dibromo-4-nitrosophenol (**IVe**) was prepared by bromination of *p*-nitrosophenol [4], 3,5-dibromo-4-nitrosophenol (**IVd**) formed from reagent **I** as a result of keeping in sulfuric acid.



I

IVc

Formerly [5] the halogen substitution by water in the concn. H_2SO_4 was observed only in the spectral concentrations (5×10^{-4} mol^{-1}l^{-1}) of 4-chloro- and 4-bromonitrosobenzenes, for in the preparative concentrations the *para*-substituted nitrosobenzenes underwent in the sulfuric acid the cyclization into the corresponding 2,6-disubstituted phenazine N-oxides [6]. Evidently the bromine atoms in compound **I** are screening the nitroso group impeding the like cyclization.

The amination of halonitrosophenols **IVa–IVc** in water or aqueous ethanol at 25–30°C with aliphatic, aromatic and alicyclic amines proceeded through the nucleophilic substitution of halogen, and the reactions involving the nitroso, hydroxy, carbonyl, and oxime groups characteristic of nitrosophenols (quinone oximes), did not occur (Scheme 2).

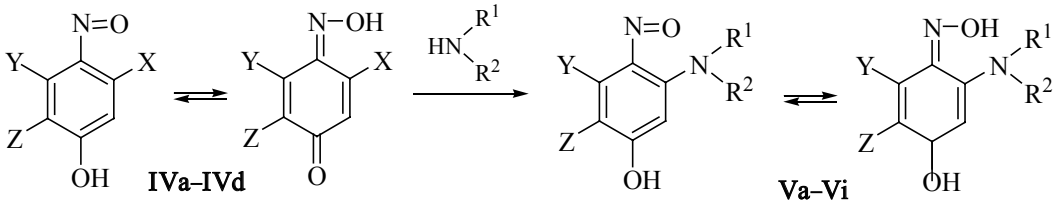
The structure and composition of compounds obtained were confirmed by physicochemical methods. The analysis of the electron absorption sprctra of compounds **V** shows that only compounds **Vg–Vi** with the absorption at 670–675 nm exist in the tautomeric nitroso form. In compounds **Va–Vf** the quinone oxime form prevails.

It is characteristic that in the amination of 2,5-dichloro-4-nitrosophenol (**IVc**) only one chlorine atom is substituted located in the *ortho*-position to the nitroso group. The substitution of just this chlorine atom is confirmed by the fact that the isomer of compound **IVd**, 2,6-dibromo-4-nitrosophenol (**IVe**) does not react with amines under mild conditions, and in more severe conditions (DMF, 90–100°C) formed a mixture of substances.

In order to understand the reactivity of compounds obtained and, in particular, the difference in the chemistry of isomeric halonitrosoarenes **IVd** and **IVe**, we performed the quantum-chemical calculations of the properties of these compounds by the density functional theory in the version of the hybrid method B3LYP/6-31G(d) [7] applying the program GAUSSIAN03 [8]. The influence of the solvent (water) was taken into account by the polarized continuum model (PCM) [9] in the version included into the program GAUSSIAN03.

The nitrosophenols are known to exist in a tautomeric

Scheme 2.



IVa–IVd **Va–Vi**

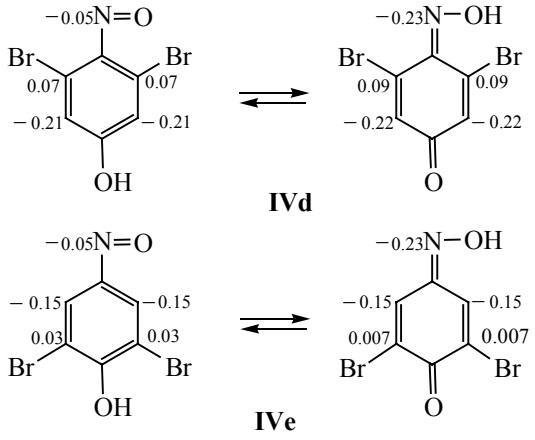
equilibrium with the quinone oximes. The position of the tautomeric equilibrium depends both on the structure of the nitrosophenol and on the solvent [10]. The introduction of substituents can affect the tautomeric equilibrium position. In turn, the reactivity of the nitrosophenols and quinone oxime toward nucleophiles is different. Therefore we first estimated the thermodynamics of the tautomerism of compounds **IVd** and **IVe**.

The calculations show that in water solutions of compounds **IVa–IVd** the nitroso form prevails. For instance, in compound **IVd** the free energy (ΔG) of the nitroso form is lower by 1.5 kcal mol^{-1}. In turn, for isomer **IVe** in water the quinone oxime form is significantly lower by the energy (ΔG –3.9 kcal mol^{-1}). Actually, the calculation results are confirmed by the electron absorption spectra. In the electronic spectra of solutions in dioxane of compounds **IVa–IVd** the characteristic for the nitroso form absorption bands $n \rightarrow \pi^*$ were registered at 750–780 nm. This band is absent from the spectrum of compound **IVe**.

It is possible to understand the direction of the nucleophilic substitution in compounds **IVa–IVd** and the essentially different properties of halonitrosoarene **IVe** (isomeric to **IVd**) analyzing the distribution of the charge and boundary electron density in these compounds [11]. All simple correlations with various reactivity indices are underlain by the "non-intersection rule" [11]. It is assumed that for similar compounds the energy ratio in tentative points on the reaction coordinate, also in the initial stage of the reaction, equals the ratio of the reaction barriers. At the same time it is possible to use the perturbation theory in the initial stage of the reaction. Under the conditions of the validity of the perturbation theory the energy of the interaction may be represented as a sum of several contributions, one of which is the Coulomb interaction of the positively charged atom of the reaction center of the electrophile and of the negative, of the nucleophile.

As seen from the figure, in both tautomers of 3,5-dibromo-4-nitrosophenol (**IVd**) a negative charge is observed on the nitrogen atom and a considerable positive charge on the carbon atoms (0.07 and 0.09) linked to bromine atoms. The substitution reaction occurs just at these carbon atoms.

In 2,6-dibromo-4-nitrosophenol (**IVe**) the positive charge on the carbon atoms linked to bromine atoms is essentially decreased in the nitroso form and virtually zero in the quinine oxime form that prevails in the water solution. Therefore compound **IVe** is less active in the reactions with nucleophiles.



Charges on atoms in the nitrosophenol and quinine oxime forms of compounds **IVd** and **IVe** calculated by the method B3LYP/6-31G(d).

Similar conclusions follow from the analysis of the boundary electron density. The contribution of the p_z-orbitals localized on the carbon atoms linked to the bromine atoms into the lowest unoccupied molecular orbital (LUMO) is considerably higher in the nitroso and quinine oxime forms of **IVd** than in the quinine oxime form **IVe**. The contribution of these orbitals into LUMO of nitroso form **IVe** is negligible.

Thus the experimental data obtained in this study are easily understood by the use of simple concepts of the indices of reactivity.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Bruker DRX-500 (500 MHz), internal reference TMS. The monitoring of the reaction progress and checking of the homogeneity of compounds obtained was performed by TLC on Silufol UV-254 plates. The melting points were measured on a Boëtius heating microblock. The electron absorption spectra in the range 550–800 nm were recorded on a spectrophotometer Evolution 300 in dioxane, measured layer thickness 1 cm, concentration 1×10^{-2} mol l^{-1}. The thermogram of compound **Vd** was obtained on an instrument NETZSCH STA 409 PC/P.

Nitrosophenols IVa–IVc, IVe were synthesized by known procedures [3, 4].

The spetrophotometric investigation of the kinetics of formation of 3,5-dibromo-4-nitrosoanilines **IIa, IIc**

was carried out in the temperature-controlled block of the spectrophotometer Evolution 300 at 29°C in DMSO using quartz cells 1 cm thick at the concentration of initial compound **I** 0.5×10^{-4} mol l^{-1}. Morpholine and *p*-toluidine were taken in exess at the concentration 10^{-3} mol l^{-1}. The accumulation of compounds **IIa, IIc** was measured at their longwave absorption maxima 431 and 432 nm respectively. The rate constants of pseudofirst order were calculated by usual method from the results of two runs for every sample that were averaged: k_{app} 115×10^{-4} (**IIa**), k_{app} 0.175×10^{-4} s^{-1} (**IIc**).

1,3-Dibromo-5-(4-methylphenyl)-2-nitrosobenzene (IIc). To a solution of 0.28 g (1 mmol) of reagent **I** in 5 ml of DMSO was added at 29°C 0.21 g (2 mmol) of 4-methylphenylamine, the mixture was stirred at the same temperature for 10–15 min. The reaction mixture was poured into water with ice. The brown precipitate was filtered off, dried, and recrystallized from ethanol. Yield 0.37 g (81%), mp 137–139°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.37 s (3H, CH_3), 6.42 s (1H, NH), 7.07 s (2H, $H^{4,6}$), 7.11 d, 7.24 d (4H, 4CH). Found, %: C 42.52; H 2.89; N 7.05. $C_{13}H_{10}Br_2N_2O$. Calculated, %: C 42.16; H 2.70; N 7.56.

1-Anilino-3-bromo-5-morpholino-2-nitrosobenzene (IIIa). To a solution of 1.14 g (3 mmol) of 1,3-dibromo-5-morpholino-2-nitrosobenzene in 10 ml of DMF was added at 20–25°C 1.4 ml (15 mmol) of aniline, the mixture was stirred at 60–70°C for 80–90 min. To the warm solution water was added dropwise. On cooling the brown precipitate was filtered off, dried, and recrystallized from DMF. Yield 1.03 g (88%), mp 197–199°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.33 t (4H, CH_2N), 3.74 t (4H, CH_2O), 6.05 d (1H, H^6, *J* 2 Hz), 6.92 d (1H, H^4, *J* 2 Hz), 7.21 t, 7.37 t (5H, 5CH), 13.44 s (1H, NH). Found, %: C 53.31; H 4.39; N 11.79. $C_{16}H_{16}BrN_3O_2$. Calculated, %: C 53.03; H 4.41; N 11.60.

1-Bromo-3-(4-methylphenyl)-5-morpholino-2-nitrosobenzene (IIIb). To a solution of 0.5 g (1.4 mmol) of 1,3-dibromo-5-morpholino-2-nitrosobenzene in 5 ml of DMF was added at 20–25°C 0.8 g (7.5 mmol) of 4-methylaniline, the mixture was stirred at 60–70°C for 80–90 min. To the warm solution water was added dropwise. On cooling the brown precipitate was filtered off, dried, and recrystallized from DMF. Yield 0.5 g (92%), mp 205–207°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 s (3H, CH_3), 3.33 t (4H, CH_2N), 3.74 t (4H, CH_2O), 6.02 d (1H, H^4, *J* 2 Hz), 6.92 d (1H, H^6, *J* 2 Hz), 7.08 d, 7.17 d (4H, 4CH, *J* 8 Hz), 13.42 s (1H, NH). Found, %: C 54.24; H 5.12; N 11.16. $C_{17}H_{18}BrN_3O_2$. Calculated, %: C 54.25; H 4.78; N 11.17.

1-Anilino-3-bromo-5-(*N,N*-dimethylamino)-2-nitrosobenzene (IIIc). To a solution of 1 g (3 mmol) of 1,3-dibromo-5-(N,N-dimethylamino)-2-nitrosobenzene in 10 ml of DMF was added at 25°C 1 ml (11 mmol) of aniline, the mixture was stirred at 60–70°C for 80–90 min. To the warm solution water was added dropwise. On cooling the brown precipitate was filtered off, dried, and recrystallized from DMF. Yield 0.62 g (60%), mp 171–172°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.04 s (6H, $2CH_3$), 5.91 d (1H, H^6, *J* 2 Hz), 6.86 d (1H, H^4, *J* 2 Hz), 7.21 t, 7.36 t (5H, 5CH), 13.51 s (1H, NH). Found, %: C 52.63; H 4.44; N 13.02. $C_{14}H_{14}BrN_3O$. Calculated, %: C 52.50; H 4.37; N 13.12.

1,3-Dianilino-5-bromo-4-nitrosobenzene (IIId). To a solution of 0.28 g (1 mmol) of 1,3-dibromo-5-morpholino-2-nitrosobenzene in 10 ml of DMF was added at 25°C 1 ml (11 mmol) of aniline, the mixture was stirred at 50–60°C for 40–50 min. The separated brown precipitate was filtered off, dried, and recrystallized from ethanol. Yield 2.66 g (68%), mp 219–221°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.27 d (1H, H^2, *J* 2 Hz), 6.41 s (1H, NH), 6.88 d (1H, H^6, *J* 2 Hz), 7.12–7.36 m (10H, 10CH), 13.49 s (1H, NH). Found, %: C 58.93; H 3.96; N 11.39. $C_{18}H_{14}BrN_2O$. Calculated, %: C 58.69; H 3.80; N 11.41.

3,5-Dibromo-4-nitrosophenol (IVd). Into 150 ml of 92% sulfuric acid was added by small portions at 0–5°C 6 g (21 mmol) of 1,3-dibromo-5-DMF-2-nitrosobenzene. The stirring was continued at the same temperature for 72 h. The solution was poured into water with ice, the yellow-brown precipitate was filtered off, washed with water, dried, and recrystallized from a mixture toluene–dioxane, 5 : 1. Yield 5.8 g (97%), mp 136–138°C. UV spectrum, λ_{max}, (ε): 782 (28). Found, %: C 26.38; H 1.08; N 4.84. $C_6H_3Br_2NO_2$. Calculated, %: C 25.62; H 1.06; N 4.98.

3-Morpholino-4-nitrosophenol (Va). To a solution of 2 ml (22 mmol) of morpholine in 15 ml of water was added at 25°C 1 g (5 mmol) of 3-bromo-4-nitrosophenol, and the mixture was stirred at 30°C for 8 h. The precipitate was separated by adding to the reaction mixture 18% hydrochloric acid till pH 6.The dark red precipitate was filtered off, dried, and recrystallized from ethanol. Yield 0.85 g (82%), mp 147–149°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.31 t (4H, CH_2N), 3.77 t (4H, CH_2O), 5.64 d (1H, H^2, *J* 2 Hz), 6.24 d.d (1H, H^6, *J* 8, 2 Hz), 7.61 d (1H, H^5, *J* 10 Hz), 11.48 s (1H, OH). Found, %: C 57.37; H 5.77; N 13.45. $C_{10}H_{12}N_2O_3$. Calculated, %: C 57.69; H 5.77; N 13.46.

Compounds **Vb–Vi** were obtained similarly.

4-Nitroso-3-piperidinophenol (Vb) was obtained from 1 ml (10 mmol) of piperidine in 4 ml of water and 0.31 g (2 mmol) of 4-nitroso-3-chlorophenol at 25°C over 9 h. Yield 0.17 g (41%), red crystals, mp 161–163°C (EtOH–H_2O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.59 s (6H, $3CH_2$), 3.32 br.s (14H, $2CH_2$), 5.56 s (1H, H^2), 6.15 d.d (1H, H^6, *J* 10, 2 Hz), 7.53 br.s (1H, H^5), 13,10 s (1H, OH). Found, %: C 64.20; H 6.72; N 13.66. $C_{11}H_{14}N_2O_2$. Calculated, %: C 64.07; H 6.79; N 13.59.

4-Nitroso-3-(4-phenylpiperazin-1-yl)phenol (Vc) was obtained from 1.62 ml (10 mmol) of 4-phenylpiperazine in 5 ml of water and 0.31 g (2 mmol) of 4-nitroso-3-chlorophenol at 25°C over 6 h. The precipitate was separated by adding to the reaction mixture 18% hydrochloric acid till pH 6. The brown precipitate was filtered off, dried, and recrystallized from ethanol. Yield 0.54 g (98%), brown crystals, mp 184–186°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.27 br.t, 3.50 br.t (8H, $4CH_2$), 5.65 s (1H, H^2), 6.19 d (1H, H^6, *J* 10 Hz), 7.56 d (1H, H^5, *J* 8 Hz), 6.80 t, 6.95 d (8 Hz), 7.23 t (5H, 5CH), 12.00–14.00 br.s (1H, OH). Found, %: C 66.45; H 5.92; N 14.28. $C_{16}H_{17}N_3O_2$. Calculated, %: C 67.84; H 6.01; N 14.84.

4-Nitroso-3-(pyrrolidin-1-yl)phenol (Vd) was obtained from 1 ml (12 mmol) of pyrrolidine in 10 ml of water and 1 g (5 mmol) of 3-bromo-4-nitrosophenol at 25°C over 7 h. Yield 0.43 g (45%), red crystals, mp 205–207°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.90 br.s, 3.50 br.s (8H, $4CH_2$), 5.24 s (1H, H^2), 6.13 d (1H, H^6, *J* 10 Hz), 7.47 br.s (1H, H^5), 12.00–13.00 br.s (1H, OH). Compound **Vd** was obtained as a crystal hydrate ($C_{10}H_{12}N_2O_2 \cdot H_2O$) as proved by the elemental analysis. Found, %: C 57.05; H 6.74; N 13.17. The thermogram of the substance showed that at 87°C the mass loss was 8.5% corresponding to the elimination of one water molecule. After heating the sample to 100°C the elemental analysis data correspond to the dehydrated form. Found, %: C 61.69; H 6.22; N 14.31. $C_{10}H_{12}N_2O_2 \cdot H_2O$. Calculated, %: C 57.14; H 6.67; N 13.33.

4-Nitroso-5-(pyrrolidin-1-yl)-2-chlorophenol (Ve) was obtained from 0.5 ml (6 mmol) of pyrrolidine in 6 ml of water and 0.5 g (2 mmol) of 4-nitroso-2,5-dichlorophenol at 25°C over 2.5 h. Yield 0.45 g (78%) red crystals, mp 208–210°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.90 m, 3.46 m (8H, $4CH_2$), 5.38 s (1H, H^6), 7.67 s (1H, H^3), 13.50 s (1H, OH). Found, %: C 52.61; H 5.42; N 11.16. $C_{10}H_{11}ClN_2O_2$. Calculated, %: C 52.98; H 4.85; N 12.36.

3-Bromo-5-morpholino-4-nitrosophenol (Vf) was obtained from 2 ml (22 mmol) of morpholine in 15 ml of water and 1 g (3.5 mmol) of 3,5-dibromo-4-nitrosophenol at 30°C over 4 h. Yield 1 g (98%), red crystals, mp 165–167°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.62 t (4H, CH_2N), 3.77 m (4H, CH_2O), 5.61 s (1H, H^6), 7.73 br.s (1H, H^2), 12.00–14.00 br.s (1H, OH). Found, %: C 42.08; H 3.72; N 9.62. $C_{10}H_{11}BrN_2O_3$. Calculated, %: C 41.81; H 3.83; N 9.75.

3-Benzylamino-5-bromo-4-nitrosophenol (Vg) was obtained from 0.4 ml (3 mmol) of benzylamine in 4 ml of water and 0.2 g (0.7 mmol) of 3,5-dibromo-4-nitrosophenol at 50°C over 8 h. Yield 0.13 g (60%), red crystals, mp 178–180°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.45 d (2H, CH_2, *J* 2 Hz), 5.95 s (1H, H^2), 6.80 s (1H, H^6), 7.29 d (*J* 6 Hz), 7.36 t (5H, 5CH), 10.00–13.00 br.s (1H, NH, 1H, OH). Found, %: C 50.53; H 3.60; N 8.37. $C_{13}H_{11}BrN_2O_2$. Calculated, %: C 50.81; H 3.58; N 9.12.

3-Bromo-4-nitroso-5-(4-toluidino)phenol (Vh) was obtained from 0.52 g (5 mmol) of *p*-toluidine in 7 ml of aqueous ethanol (1:1) and 0.46 g (1.6 mmol) of 3,5-dibromo-4-nitrosophenol at 25°C over 2 h. Yield 0.44 g (88%), red crystals, mp 207–209°C (EtOH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.33 s (3H, CH_3), 6.14 s (1H, H^6), 6.88 d (1H, H^2, *J* 2 Hz), 7.20 d, 7.27 d (4H, 4CH, *J* 8 Hz), 12.00–13.00 br.s (1H, NH, 1H, OH). Found, %: C 50.79; H 3.75; N 9.50. $C_{13}H_{11}BrN_2O_2$. Calculated, %: C 50.81; H 3.58; N 9.12.

3-Bromo-5-isobutylamino-4-nitrosophenol (Vi) was obtained from 0.45 ml (4.5 mmol) of isobutylamine in 18 ml of water and 0.5 g (1.75 mmol) of 3,5-dibromo-4-nitrosophenol at 35°C over 4.5 h. Yield 0.22 g (46%), orange crystals, mp 158–160°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.93 t (6H, $2CH_3$), 1.86–1.89 m (1H, CH), 3.05 t (2H, CH_2), 6.07 br.s (1H, H^6), 6.81 br.s (1H, H^2), 10.00–13.00 br.s (1H, OH, 1H, NH). Found, %: C 44.04; H 4.77; N 10.55. $C_{10}H_{14}BrN_2O_2$. Calculated, %: C 43.79; H 5.11; N 10.21.

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