Organic Chemistry

Selective reduction of the nitro group in the presence of the azoxy group. Synthesis of 2-(alkyl-*NNO*-azoxy)anilines

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Tin(II) chloride selectively reduces the aromatic nitro group to the amino group, the azoxy group remaining intact. This allows the preparation of 2-(R-*NNO*-azoxy)anilines from 2-(R-*NNO*-azoxy)nitrobenzenes bearing electron-donating or weak electron-withdrawing substituents (Me or Br) in the benzene ring and alkyl substituents at the distal N atom of the azoxy group. The presence of electron-withdrawing substituents at the azoxy group (for example, CO_2Et) leads to a change in the direction of the reaction resulting in selective reduction of the azoxy group to the hydrazo group.

Key words: nitrosobenzenes, nitrobenzenes, anilines, azoxy compounds, reduction of the nitro group.

Anilines containing the R-*NNO*-azoxy group in the *ortho* position can serve as the starting compounds for the construction of various heterocyclic skeletons. Thus compounds of the benzo-1,2,3,4-tetrazine series (benzo-1,2,3,4-tetrazine 1,3-dioxides,[1] benzo-1,2,3,4-tetrazine 1-oxides,[2] 2-(*tert*-butyl)-6-oxo-2,6-dihydrobenzo-1,2,3,4-tetrazine 4-oxides,[3] and benzoditetrazine tetroxides[4]) and 1-hydroxybenzo-1,2,3-triazole 3-oxides[5] were synthesized from 2-(*tert*-butyl-*NNO*-azoxy)anilines.

Anilines of the above-mentioned type can be prepared[6] from *ortho*-bromo-(*tert*-butyl-*NNO*-azoxy)benzenes containing electron-withdrawing substituents in the ring by nucleophilic replacement of bromine by reaction with ammonia. However, this procedure is unsuitable for compounds containing electron-donating substituents. In this case, the corresponding nitro compounds can serve as precursors of anilines. Previously,[1,6] we have found that 2-(*tert*-butyl-*NNO*-azoxy)aniline can be synthesized by selective reduction of the nitro group in 2-(*tert*-butyl-*NNO*-azoxy)nitrobenzene with $SnCl_2$. The aim of the present study was to reveal the scope of the selective reduction of the nitro group in the presence of the azoxy group.

Results and Discussion

Synthesis of the starting compounds. The approach to (azoxy)nitrobenzenes is based on the oxidation of the corresponding nitroanilines **1** to nitroso compounds **2** followed by the reactions with *N*,*N*-dibromoamines according to the Kovacic method[7] (Scheme 1).

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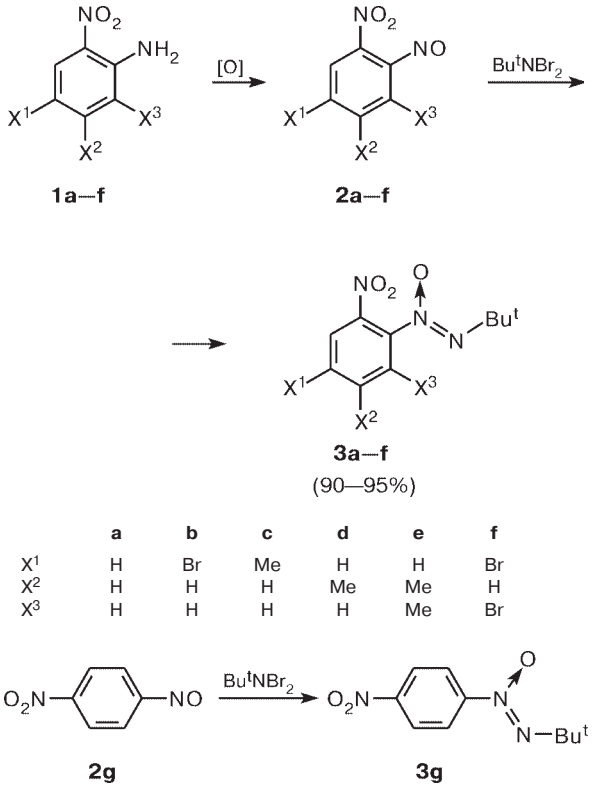
Scheme 1



Nitrosobenzenes **2a,b** were prepared by oxidation of the corresponding anilines **1a,b** with Caro's acid (*cf.* lit. data[8]), compounds **2c,d** were obtained by oxidation of neutralized Caro's acid (*cf.* lit. data[9]), and *ortho*,*ortho*-disubstituted nitrosobenzene **2e** was synthesized by oxidation with 30% H_2O_2 (*cf.* lit. data[10]). Oxidation of weakly basic aniline **1f** presented the most substantial difficulties. Standard methods failed and it was possible to prepare compound **2f** only by oxidation with a calculated amount of trifluoroperacetic acid.*

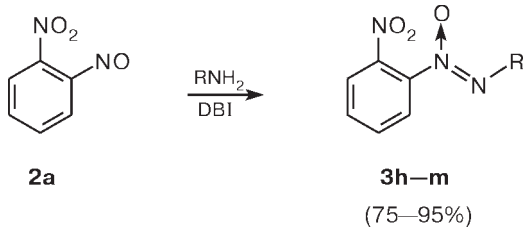
Solutions of all the resulting nitroso compounds in organic solvents were green-colored. The ^{1}H NMR spectra of all these compound, except for **2e**, have one set of signals corresponding to the monomeric forms. In the spectrum of nitroso compound **2e**, signals belonging to the dimer are observed along with signals corresponding to the monomer. The amount of the dimer increased as the temperature was lowered (33% at 297 K and 75% at 273 K).

Nitro compounds **3a—g** containing different substituents X in the benzene ring (see Scheme 1) were synthesized from the corresponding nitrosobenzenes **2a—g** and *N*,*N*-dibromo-*tert*-butylamine prepared beforehand.

* Trifluoroperacetic acid was first used for oxidation of weakly basic *ortho*,*ortho*-disubstituted anilines to nitroso compounds in our previous study.[11]

Compounds **3h—m** (Scheme 2) bearing different substituents R at the distal N atom of the azoxy group were synthesized starting from *N*,*N*-dibromoamines, which were generated *in situ* from the amine or its salt and dibromoisocyanuric acid (DBI) as the brominating agent (*cf.* lit. data[12]). It should be noted that 2,4,6-trichloroaniline and 3-amino-4-methylfurazan did not give stable *N*,*N*-dibromo derivatives and the mechanism of formation of the azoxy group in these processes is, conceivably, different from the mechanism of the Kovacic reaction.

Scheme 2

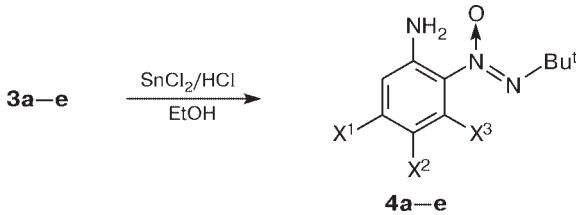


3: R = Me (**h**); Pr^i (**i**); 1-Ad (**j**); 2,4,6-$Cl_3C_6H_2$ (**k**); 4-methylfurazan-3-yl (**l**); CO_2Et (**m**)

Reduction of nitro compounds. The nitro and azoxy groups are generally reduced with the same reagents under similar conditions.[13] Reliable data on selective reduction of the nitro group in the presence of the azoxy group are lacking in the literature. Our attempts to reduce compound **2a** using reducing agents usually employed for the reduction of the nitro group (Fe/HCl, Zn/AcOH, N_2H_4/Raney Ni, or H_2S) afforded complex mixtures of products.

We succeeded in performing selective reduction of the nitro group in *ortho*-(*tert*-butyl-*NNO*-azoxy)nitrobenzenes **3a—e** under the action of $SnCl_2$ in the presence of HCl. The reactions gave rise to the corresponding anilines **4a—e** in 69—95% yields (Scheme 3, Table 1).

Scheme 3



	a	b	c	d	e
X^1	H	Br	Me	H	H
X^2	H	H	H	Me	Me
X^3	H	H	H	H	Me

Substituents in the benzene ring, which are either electron-donating (Me in compounds **3c—e**) or weak elec-

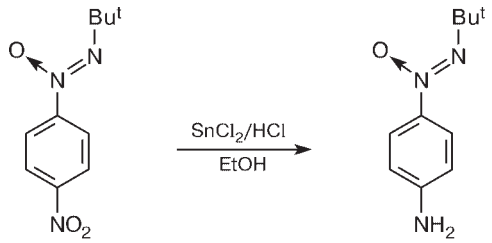
Table 1. Reduction of (azoxy)nitrobenzenes **3**

Starting compound	[**3**] /mol L^{-1}	t [a]/h	Reaction product	Yield (%)	Purification technique[b]
3a	0.35	2	**4a**	69	*A*
3b	0.50	3.5	**4b**	95	*B*, *C*
3c	0.15	3	**4c**	78	*A*
3d	0.15	3	**4d**	90	*A*
3e	0.16	3	**4e**	82	*A*
3f	0.19	4	**5**	36	*B*, *C*
3g	0.19	2	**4g**	93	*A*
3h	0.37	1	**4h**	81	*B*, *C*
3i	0.19	2.5	**4i**	82	*A*, *D*
3j	0.16	2.5	**4j**	90	*A*
3k	0.06	4	**4k**	10	*B*, *C*
3m	0.18	2	**6**	93	—[c]

[a] Reaction time.
[b] See Experimental.
[c] The product was isolated without additional purification.

tron-withdrawing (Br in compound **3b**), have no effect on the selectivity of reduction. The *ortho* arrangement of the nitro and azoxy groups is not essential. Thus only the nitro group is reduced in compound **3g** in which the nitro group is at the *para* position with respect to the azoxy group (Scheme 4).

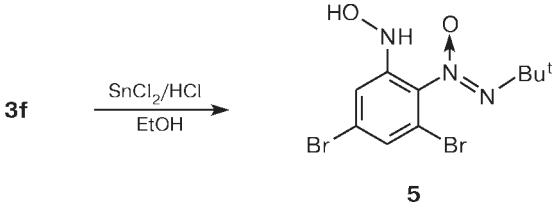
Scheme 4



3g **4g**

In the case of reduction of dibromo-substituted compound **3f**, the nitro group was transformed into the hydroxyamino group after which the process was stopped (Scheme 5). Under more drastic conditions, hydroxylamine **5** was obtained in lower yield, but reduction to amine did not take place. The reasons for high resistance of the hydroxyamino group in compound **5** to reduction remain unclear.

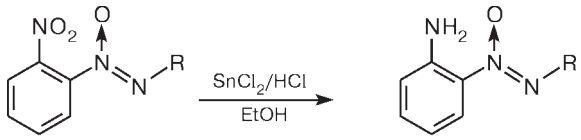
Scheme 5



5

Variations in aliphatic substituents at the distal N atom of the azoxy group (R = Me, Pr^i, Bu^t, or 1-Ad) have virtually no effect on the yields of amines **4** (Scheme 6, Table 1). The electron-withdrawing 2,4,6-trichlorophenyl group in compound **3k** diminishes the yield of the target amine to 10%, whereas reduction of (azoxy)nitrobenzene **3l** (R = 4-methylfurazan-3-yl) afforded a mixture of products among which the target amine was not detected.

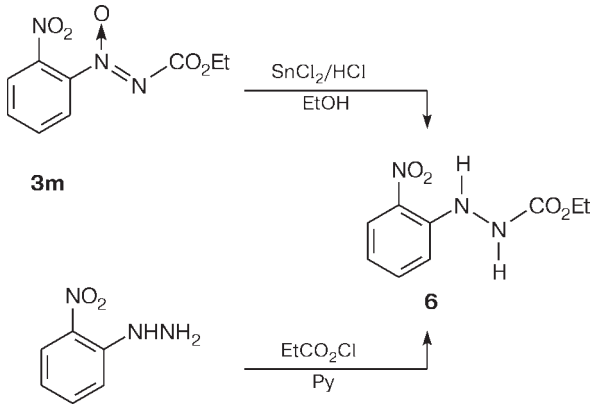
Scheme 6



3a,h—l **4a,h—k**

In the presence of the ethoxycarbonyl substituent at the distal N atom of the azoxy group, the regioselectivity of the reaction changes radically: the nitro group remained intact, while the azoxy group was reduced to the hydrazo group to form compound **6** (Scheme 7). The physicochemical and spectroscopic characteristics of this compound are identical with those for a sample[14] prepared by the independent synthesis from *ortho*-nitrophenylhydrazine and ethyl chloroformate.

Scheme 7



3m **6**

^{14}N NMR spectroscopy is a convenient method for the analysis of the purity of the reaction products and selectivity of reduction (Table 2) because the signals of the azoxy and nitro groups are rather narrow and are clearly seen in the spectra. These signals are located in the known region and the chemical shifts depend only slightly on the nature of the substituents (δ_N for the NO_2 and

Table 2. ^{14}N NMR spectra (in acetone-d_6) of (azoxy)nitrobenzenes **3a—m** and their reduction products

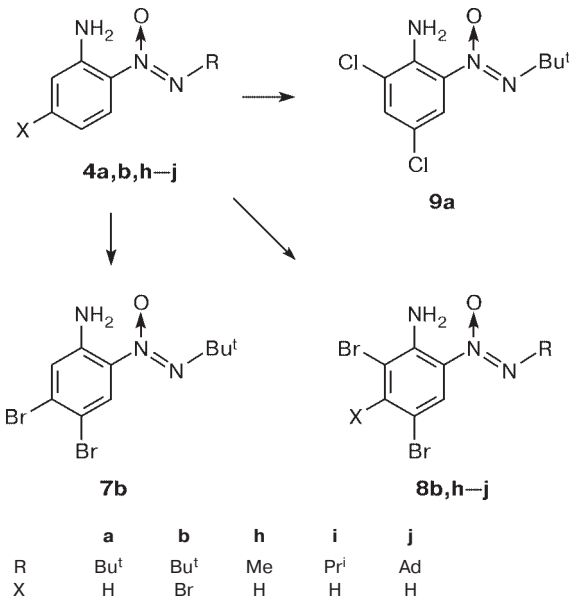
Starting compound	δ_N ($\Delta\nu_{1/2}$/Hz)		Product	δ_N ($\Delta\nu_{1/2}$/Hz)	
	N(O)=N	NO_2		N(O)=N	NH_2
3a[a]	−56 (30)	−14 (50)	**4a**[a]	−48 (100)	−323 (800)
3b	−58 (40)	−17 (50)	**4b**	−49 (130)	−319 (1300)
3c	−56 (130)	−15 (210)	**4c**	−46 (90)	−316 (700)
3d	−55 (90)	−15 (140)	**4d**	−46 (100)	−326 (650)
3e	−56 (130)	−15 (150)	**4e**	−48 (150)	—
3f	−62 (90)	−21 (140)	**5**	−57 (150)	—
3g	−55 (450)	−15 (190)	**4g**	−51 (180)	—
3h	−52 (70)	−14 (90)	**4h**	−43 (90)	−321 (500)
3i	−59 (80)	−17 (90)	**4i**	−50 (130)	−319 (600)
3j	−50 (40)	−14 (50)	**4j**	−47 (160)	−322 (850)
3k	−50 (90)	−16 (80)	**4k**	−41 (180)	−324 (750)
3l	−50 (70)	−15 (60)	—	—	—
3m	−50 (40)	−16 (50)	**6**	—	−9 (110)[b]

[a] See lit. data.[6]
[b] For the NO_2 group.

RN=N(O) groups (R = Ar, Alk, or COOR) range from −14 to −21 and from −41 to −62, respectively).

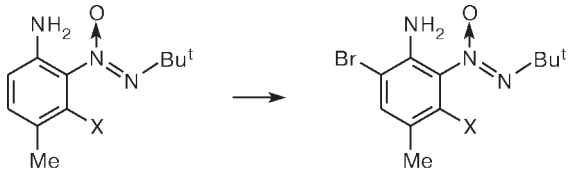
2-Azoxyanilines containing the halogen atoms in the *ortho* and *para* positions are more conveniently prepared by halogenation of the corresponding anilines **4** (Scheme 8) rather than by reduction of 2-(azoxy)nitrobenzenes. Thereby, the range of compounds of this class can be substantially extended.

Scheme 8



Bromination of anilines with 1 equiv. of Br_2 in AcOH in the presence of AcONa or with 1 equiv. of NBS afforded *para*-bromo-substituted anilines (for example, **4b** → **7b**) (see Scheme 8). In these cases, the *ortho*-bromo-substituted isomer was formed only in trace amounts. *ortho*-Bromination takes place if the *para* position is substituted (**4d,e** → **7d,e**) (Scheme 9). Under the action of 2 equiv. of the brominating reagent, the *ortho*,*para*-dibromo derivatives were obtained (**4b,h—j** → **8b,h—j**) (see Scheme 8). A mixture of hydrochloric acid and 30% H_2O_2 is a convenient reagent for chlorination of anilines. According to this procedure, dichloroaniline **9a** was prepared from aniline **4a** in a yield higher than 60% (see Scheme 8).

Scheme 9



4d,e **7d,e**

X = H (**d**), Me (**e**)

Thus, the aromatic nitro group is selectively reduced to the amino group in the presence of the azoxy group only if the distal N atom of the latter bears electron-donating alkyl substituents. In the presence of the electron-withdrawing substituent, such as CO_2Et, the regioselectivity of the reaction changes and the azoxy group is selectively reduced to the hydrazo group. The reactions involving compounds with aryl or hetaryl substituents (R = 2,4,6-$Cl_3C_6H_2$ or 4-methylfurazan-3-yl) produce mixtures of products. In the latter case, the rate of reduction of the nitro group is apparently comparable to that of the azoxy group.

Experimental

The IR spectra were recorded on a Specord M-80 spectrometer. The mass spectra were obtained on a Kratos MS-30 instrument (EI, 70 eV); for the chlorine- and bromine-containing fragments, only the peaks for the ^{35}Cl and ^{79}Br isotopes are reported. The ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were measured on a Bruker AM-300 spectrometer operating at 300.13, 75.5, 21.5, and 30.4 MHz, respectively. The chemical shifts in the ^{14}N and ^{15}N NMR spectra are given in the δ scale relative to $MeNO_2$. The course of the reactions was monitored by TLC on Silufol UV-254 plates; silica gel was used for column chromatography. *o*-Nitronitrosobenzene (**2a**),[8] *p*-nitronitrosobenzene (**2g**),[8] 4-methyl-2-nitronitrosobenzene (**2c**),[9] *N*,*N*-dibromo-*tert*-butylamine,[15] and 2-(*tert*-butyl-*NNO*-azoxy)nitrobenzene (**3a**)[6] were prepared according to procedures described previously.

4-Bromo-2-nitronitrosobenzene (2b). A solution of Caro's acid, which was prepared from concentrated H_2SO_4 (7 mL) and ammonium peroxydisulfate (18.2 g, 0.08 mol) followed by dilu-

tion with water to 50 mL, was added with stirring to a suspension of 4-bromo-2-nitroaniline (**1b**) (6.6 g, 30 mmol) in concentrated H_2SO_4 (7.5 mL) and water (1.2 mL). The reaction mixture was stirred at 20 °C for 5 h and then kept for one day without stirring. The precipitate that formed was filtered off, thoroughly washed on a filter with water, and dried in air. Compound **2b** was obtained in a yield of 1.6 g (23%) as yellow crystals, m.p. 128—130 °C. Found (%): C, 31.32; H, 1.37; Br, 34.76; N, 12.01. $C_6H_3BrN_2O_3$. Calculated (%): C, 31.20; H, 1.31; Br, 34.59; N, 12.13. IR (KBr), ν/cm^{-1}: 1540, 1350 (NO_2). ^{1}H NMR ($CDCl_3$), δ: 6.36 (d, 1 H, J = 8.7 Hz); 7.8 (dd, 1 H, J = 8.7 Hz, J = 2.0 Hz); 8.21 (d, 1 H, J = 2.0 Hz). ^{14}N NMR ($CDCl_3$), δ: −17.2 (NO_2, $\Delta\nu_{1/2}$ = 80 Hz). MS, m/z: 230 [M]$^+$.

5-Methyl-2-nitronitrosobenzene (2d). A neutralized solution of Caro's acid, which was prepared from concentrated H_2SO_4 (16 mL) and ammonium peroxydisulfate (22 g, 0.1 mol) followed by dilution to 300 mL and neutralization with a concentrated ammonia to pH 6, was added with stirring to a solution of 5-methyl-2-nitroaniline (**1d**) (2.28 g, 15 mmol) in dioxane (25 mL). The reaction mixture was kept at 20 °C for two days. The precipitate that formed was filtered off, washed on a filter with water, and recrystallized from C_6H_6. Compound **2d** was obtained in a yield of 0.7 g (28%) as pale-yellow crystals, m.p. 138—140 °C (with decomp.). Found (%): C, 50.22; H, 3.41; N, 16.98. $C_7H_6N_2O_3$. Calculated (%): C, 50.61; H, 3.64; N, 16.86. IR (KBr), ν/cm^{-1}: 1520, 1350 (NO_2). ^{1}H NMR (acetone-d_6), δ: 2.26 (s, 3 H); 6.45 (d, 1 H, J = 1.2 Hz); 7.88 (dd, 1 H, J = 8.5 Hz, J = 1.2 Hz); 8.17 (d, 1 H, J = 8.5 Hz). ^{13}C NMR (acetone-d_6), δ: 21.3, 111.7, 125.2, 127.4, 133.9, 137.1, 146.3. ^{14}N NMR (acetone-d_6), δ: −8.5 (NO_2, $\Delta\nu_{1/2}$ = 140 Hz). MS, m/z: 166 [M]$^+$.

2,3-Dimethyl-6-nitronitrosobenzene (2e). A 30% aqueous solution of H_2O_2 (8 mL) was added with stirring to a solution of 2,3-dimethyl-6-nitroaniline (**1e**) (1.66 g, 10 mmol) in AcOH (40 mL) and H_2SO_4 (2 mL) and then the reaction mixture was stirred at 20 °C for 12 h. The product that precipitated was filtered off, washed on a filter with water, and dried in air. Compound **2e** was obtained in a yield of 0.67 g (38%) as lemon-yellow crystals, m.p. 144—146 °C. Found (%): C, 53.46; H, 4.32; N, 15.81. $C_8H_8N_2O_3$. Calculated (%): C, 53.33; H, 4.48; N, 15.55. IR (KBr), ν/cm^{-1}: 1530, 1360 (NO_2). In the ^{1}H NMR spectrum (acetone-d_6), the monomer **2e** : dimer **2e** ratios were 2 : 1 and 1 : 3 at 25 and 0 °C, respectively. ^{1}H NMR of monomer **2e** (acetone-d_6, 25 °C), δ: 2.71 and 2.88 (both s, 3 H each); 7.50 and 7.78 (both d, 1 H each, J = 8.1 Hz). ^{1}H NMR of dimer **2e** (acetone-d_6, 0 °C), δ: 2.44 and 2.52 (both s, 3 H each); 7.70 and 8.02 (both d, 1 H each, J = 8.1 Hz). ^{14}N NMR of monomer **2e** (acetone-d_6, 25 °C), δ: −8.8 (NO_2, $\Delta\nu_{1/2}$ = 60 Hz). ^{14}N NMR of dimer **2e** (acetone-d_6, 0 °C), δ: −12.4 (NO_2, $\Delta\nu_{1/2}$ = 220 Hz). MS, m/z: 180 [M]$^+$.

2,4-Dibromo-6-nitronitrosobenzene (2f). Trifluoroacetic anhydride $(CF_3CO)_2O$ (0.71 mL, 3.5 mmol) was added to a stirred mixture of CH_2Cl_2 (5 mL) and 80% aqueous H_2O_2 (0.15 mL) at 0 °C. The reaction mixture was kept for 10 min and then slowly added with stirring to a solution of 2,4-dibromo-6-nitroaniline (**1f**) (0.5 g, 1.7 mmol) in CH_2Cl_2 (10 mL) at 20 °C. Then the reaction mixture was stirred for 2 h and washed with a solution of $NaHCO_3$ (2×10 mL). The organic layer was dried with $MgSO_4$ and the solvent was evaporated. Compound **2f** was obtained in a yield of 0.5 g (95%) as bright-yellow crystals, m.p. 72—74 °C. Found (%): C, 23.20; H, 0.67; Br, 51.98; N, 9.41. $C_6H_2Br_2N_2O_3$. Calculated (%): C, 23.25; H, 0.65; Br, 51.57; N, 9.04. IR (KBr), ν/cm^{-1}: 1540, 1340 (NO_2). ^{1}H NMR (acetone-d_6), δ: 8.15 and 8.58 (both br.s, 1 H each). ^{14}N NMR (acetone-d_6), δ: −16.9 (NO_2, $\Delta\nu_{1/2}$ = 220 Hz). MS, m/z: 308 [M]$^+$.

Preparation of azoxy compounds 3b—g by reactions of nitrosobenzenes 2b—g with *N,N*-dibromo-*tert*-butylamine (general procedure). Dibromo-*tert*-butylamine Bu^tNBr_2 (1.28 g, 5.25 mmol) was added with stirring to a solution of a nitroso compound (5 mmol) in CH_2Cl_2 (220 mL). The reaction mixture was kept for ~16 h and then the solvent was evaporated. The products were purified by column chromatography when needed.

1-(4-Bromo-2-nitrophenyl)-2-(*tert*-butyl)diazene 1-oxide (3b). M.p. 57—59 °C. Found (%): C, 39.57; H, 4.11; Br, 26.57; N, 13.82. $C_{10}H_{12}BrN_3O_3$. Calculated (%): C, 39.75; H, 4.00; Br, 26.45; N, 13.91. IR (KBr), ν/cm^{-1}: 1540, 1350 (NO_2); 1490 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 1.41 (s, 9 H); 7.88 (d, 1 H, J = 8.8 Hz); 8.09 (dd, 1 H, J = 8.8 Hz, J = 2.2 Hz); 8.26 (d, 1 H, J = 2.2 Hz). ^{13}C NMR (acetone-d_6), δ: 25.4, 60.8, 124.5, 127.8, 128.5, 137.6. MS, m/z: 301 [M]$^+$.

2-(*tert*-Butyl)-1-(4-methyl-2-nitrophenyl)diazene 1-oxide (3c). M.p. 35—38 °C. Found (%): C, 55.84; H, 6.35; N, 18.36. $C_{11}H_{15}N_3O_3$. Calculated (%): C, 55.69; H, 6.37; N, 17.71. IR (thin layer), ν/cm^{-1}: 1540, 1360 (NO_2); 1490 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 1.45 (s, 9 H); 2.61 (s, 3 H); 7.5 (d, 1 H, J = 8.1 Hz); 7.62 (dd, 1 H, J = 8.1 Hz, J = 2.2 Hz); 7.68 (d, 1 H, J = 2.2 Hz). ^{13}C NMR (acetone-d_6), δ: 21.4, 25.8, 61.0, 125.7, 125.9, 134.8, 141.4. MS, m/z: 237 [M]$^+$.

2-(*tert*-Butyl)-1-(5-methyl-2-nitrophenyl)diazene 1-oxide (3d). Yellow oil. Found (%): C, 55.60; H, 6.32; N, 17.83. $C_{11}H_{15}N_3O_3$. Calculated (%): C, 55.69; H, 6.37; N, 17.71. IR (thin layer), ν/cm^{-1}: 1540, 1360 (NO_2); 1480 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 1.45 (s, 9 H); 2.47 (s, 3 H); 7.59 (dd, 1 H, J = 8.3 Hz, J = 2.1 Hz); 7.66 (d, 1 H, J = 2.1 Hz); 7.96 (d, 1 H, J = 8.3 Hz). MS, m/z: 237 [M]$^+$.

2-(*tert*-Butyl)-1-(2,3-dimethyl-6-nitrophenyl)diazene 1-oxide (3e). M.p. 64—66 °C. Found (%): C, 57.35; H, 6.85; N, 16.93. $C_{12}H_{17}N_3O_3$. Calculated (%): C, 57.36; H, 6.82; N, 16.72. IR (KBr), ν/cm^{-1}: 1530, 1340 (NO_2); 1500 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 1.46 (s, 9 H); 2.25 and 2.46 (both s, 3 H each); 7.53 (d, 1 H, J = 8.8 Hz). ^{13}C NMR (acetone-d_6), δ: 13.8, 20.7, 25.6, 60.7, 123.2, 123.9, 131.1, 132.7, 140.8, 147.2. MS, m/z: 251 [M]$^+$.

2-(*tert*-Butyl)-1-(2,4-dibromo-6-nitrophenyl)diazene 1-oxide (3f). M.p. 77—79 °C. Found (%): C, 31.66; H, 2.92; Br, 42.51; N, 10.84. $C_{10}H_{11}Br_2N_3O_3$. Calculated (%): C, 31.52; H, 2.91; Br, 41.94; N, 11.03. IR (KBr), ν/cm^{-1}: 1520, 1370 (NO_2); 1500 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 1.48 (s, 9 H); 8.42 and 8.57 (both d, 1 H each, J = 2.2 Hz). ^{13}C NMR (acetone-d_6), δ: 25.6, 61.9, 116.9, 119.3, 128.7, 142.2. MS, m/z: 379 [M]$^+$.

2-(*tert*-Butyl)-1-(4-nitrophenyl)diazene 1-oxide (3g). M.p. 97—99 °C. Found (%): C, 53.62; H, 5.82; N, 18.91. $C_{10}H_{13}N_3O_3$. Calculated (%): C, 53.80; H, 5.87; N, 18.82. IR (KBr), ν/cm^{-1}: 1530, 1340 (NO_2); 1480 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 1.49 (s, 9 H); 8.38 (m, 4 H). ^{13}C NMR (acetone-d_6), δ: 25.7, 60.0, 124.4, 125.2, 125.9, 150.4. MS, m/z: 223 [M]$^+$.

Preparation of azoxy compounds 3h—m by reactions of *o*-nitronitrosobenzene (2a) with amines and DBI (general procedure). Amine (in the case of **3j—m**) or its salt (in the case of **3h—i**) (3 mmol) and DBI (0.9 g, 3.3 mmol) were added with stirring to a solution of *o*-nitronitrosobenzene (**2a**) (0.41 g,

2.7 mmol) in MeCN (20 mL) and then the reaction mixture was stirred at 20 °C for 5 h (**3h,j,m**) or 10 h (**3i,k,l**). The precipitate of cyanuric acid was filtered off, the filtrate was concentrated to dryness, and the product was extracted from the solid residue with CH_2Cl_2 or light petroleum. Azoxy compounds **3h—m** were purified by column chromatography on silica gel when needed.

2-Methyl-1-(2-nitrophenyl)diazene 1-oxide (3h). Red-orange oil. Found (%): C, 46.35; H, 3.85; N, 22.86. $C_7H_7N_3O_3$. Calculated (%): C, 46.41; H, 3.89; N, 23.20. IR (KBr), ν/cm^{-1}: 1540, 1350 (NO_2); 1500 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 3.38 (s, 3 H); 7.83 (m, 1 H); 7.91 (m, 2 H); 8.07 (m, 1 H). MS, *m/z*: 181 [M]$^+$.

2-Isopropyl-1-(2-nitrophenyl)diazene 1-oxide (3i). Orange-yellow oil. Found (%): C, 51.62; H, 5.35; N, 20.86. $C_9H_{11}N_3O_3$. Calculated (%): C, 51.67; H, 5.30; N, 20.09. IR (thin layer), ν/cm^{-1}: 1540, 1350 (NO_2); 1480 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 1.26 (d, 6 H, *J* = 5.9 Hz); 4.26 (sept, 1 H, *J* = 5.9 Hz); 7.86 (m, 2 H); 8.04 (m, 2 H). ^{13}C NMR (acetone-d_6), δ: 19.3, 53.1, 127.9, 128.6, 134.5, 137.6, 141.5, 144.6. MS, *m/z*: 209 [M]$^+$.

2-(Adamantan-1-yl)-1-(2-nitrophenyl)diazene 1-oxide (3j). M.p. 163—166 °C. Found (%): C, 64.21; H, 6.35; N, 13.61. $C_{16}H_{19}N_3O_3$. Calculated (%): C, 63.77; H, 6.36; N, 13.94. IR (KBr), ν/cm^{-1}: 1540, 1350 (NO_2); 1490 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 1.76 (m, 6 H); 2.12 (m, 3 H); 2.18 (m, 6 H); 7.76 (m, 1 H); 7.85 (m, 2 H); 8.04 (m, 1 H). ^{13}C NMR (acetone-d_6), δ: 30.1, 36.2, 37.9, 62.0, 125.7, 126.1, 132.0, 134.7. MS, *m/z*: 301 [M]$^+$.

2-Ethoxycarbonyl-1-(2-nitrophenyl)diazene 1-oxide (3k). M.p. 117—119 °C. Found (%): C, 45.60; H, 3.75; N, 17.87. $C_9H_9N_3O_5$. Calculated (%): C, 45.19; H, 3.79; N, 17.57. IR (KBr), ν/cm^{-1}: 1540, 1340 (NO_2); 1510 (N(O)=N); 1680 (C=O). ^{1}H NMR (acetone-d_6), δ: 1.38 (t, 3 H, *J* = 7.4 Hz); 4.44 (q, 2 H, *J* = 7.4 Hz); 7.95 (m, 2 H); 8.07 (m, 1 H); 8.16 (m, 1 H). ^{13}C NMR (acetone-d_6), δ: 14.4, 65.4, 126.4, 134.2, 135.2, 141.2, 143.8, 156.9. MS, *m/z*: 239 [M]$^+$.

1-(2-Nitrophenyl)-2-(2,4,6-trichlorophenyl)diazene 1-oxide (3l). M.p. 123—125 °C. Found (%): C, 41.67; H, 1.72; Cl, 31.23; N, 12.26. $C_{12}H_6Cl_3N_3O_3$. Calculated (%): C, 41.59; H, 1.72; Cl, 30.69; N, 12.13. IR (KBr), ν/cm^{-1}: 1540, 1340 (NO_2); 1470 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 7.68 (s, 2 H); 8.01 and 8.21 (both m, 2 H each). ^{13}C NMR (acetone-d_6), δ: 126.4, 126.9, 129.5, 129.7, 134.1, 134.5, 135.0, 138.8, 141.5, 144.1. MS, *m/z*: 345 [M]$^+$.

2-(4-Methylfurazan-3-yl)-1-(2-nitrophenyl)diazene 1-oxide (3m). M.p. 58—60 °C. Found (%): C, 43.61; H, 2.85; N, 28.56. $C_9H_7N_5O_4$. Calculated (%): C, 43.38; H, 2.83; N, 28.11. IR (KBr), ν/cm^{-1}: 1540, 1360 (NO_2); 1490 (N(O)=N). ^{1}H NMR (acetone-d_6), δ: 2.46 (s, 3 H); 8.04 and 8.24 (both m, 2 H each). ^{13}C NMR (acetone-d_6), δ: 8.6, 126.4, 126.9, 134.3, 135.3, 142.1, 144.1, 150.2, 155.9. MS, *m/z*: 249 [M]$^+$.

Reduction of nitrobenzenes 3a—m with $SnCl_2$ (general procedure). A solution of $SnCl_2 \cdot 2H_2O$ (7 mmol) in concentrated HCl (6.3 mL) was added with stirring to a solution of nitro compounds **3a—m** (2 mmol) in EtOH, whereupon the reaction mixture slightly warmed up. Then the mixture was stirred at 20 °C until the starting compound disappeared completely (see Table 1) and poured into water (a tenfold excess with respect to EtOH). The solution was alkalified to pH 7—8 and extracted with AcOEt (*A*) or extracted from an acidic solution (*B*). The extract was washed with brine and dried with $MgSO_4$. The solvent was evaporated. In some cases, the products were purified by chromatography on silica gel ($CHCl_3$ (*C*) or C_6H_6 (*D*) as the eluent).

1-(2-Aminophenyl)-2-(*tert*-butyl)diazene 1-oxide (4a) was identical with the authentic sample, m.p. 30—32 °C (lit. data[2]: m.p. 30—31 °C).

1-(2-Amino-4-bromophenyl)-2-(*tert*-butyl)diazene 1-oxide (4b) was identical with the authentic sample, m.p. 81—83 °C (lit. data[2]: m.p. 81.5—82 °C).

1-(2-Amino-4-methylphenyl)-2-(*tert*-butyl)diazene 1-oxide (4c). Orange-yellow oil. Found (%): C, 63.78; H, 8.25; N, 20.39. $C_{11}H_{17}N_3O$. Calculated (%): C, 63.74; H, 8.27; N, 20.27. IR (KBr), ν/cm^{-1}: 1480 (N(O)=N); 3340, 3460 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.45 (s, 9 H); 2.24 (s, 3 H); 6.3 (br.s, 2 H); 6.45 (dd, 1 H, *J* = 8.8 Hz, *J* = 1.7 Hz); 6.71 (d, 1 H, *J* = 1.7 Hz); 7.82 (d, 1 H, *J* = 8.8 Hz). ^{13}C NMR (acetone-d_6), δ: 21.2, 26.3, 59.2, 117.5, 118.6, 125.1, 133.2, 142.7. MS, *m/z*: 207 [M]$^+$.

1-(2-Amino-5-methylphenyl)-2-(*tert*-butyl)diazene 1-oxide (4d). M.p. 78—80 °C. Found (%): C, 63.56; H, 8.21; N, 20.30. $C_{11}H_{17}N_3O$. Calculated (%): C, 63.74; H, 8.27; N, 20.27. IR (thin layer), ν/cm^{-1}: 1470 (N(O)=N); 3350, 3460 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.46 (s, 9 H); 2.23 (s, 3 H); 6.10 (br.s, 2 H); 6.81 (d, 1 H, *J* = 8.5 Hz); 7.02 (dd, 1 H, *J* = 8.5 Hz, *J* = 1.7 Hz); 7.69 (d, 1 H, *J* = 1.7 Hz). MS, *m/z*: 207 [M]$^+$.

1-(2-Amino-5,6-dimethylphenyl)-2-(*tert*-butyl)diazene 1-oxide (4e). M.p. 100—102 °C. Found (%): C, 65.28; H, 8.75; N, 18.41. $C_{12}H_{19}N_3O$. Calculated (%): C, 65.13; H, 8.65; N, 18.99. IR (KBr), ν/cm^{-1}: 1480 (N(O)=N); 3340, 3430 (NH_2). ^{1}H NMR (DMSO-d_6), δ: 1.44 (s, 9 H); 2.00 (s, 3 H); 2.13 (s, 1 H); 4.60 (br.s, 2 H); 6.61 and 6.82 (both d, 1 H each, *J* = 8.1 Hz). ^{13}C NMR (DMSO-d_6), δ: 13.3, 18.7, 25.4, 59.0, 113.9, 124.5, 128.0, 130.0, 136.7, 137.8. MS, *m/z*: 221 [M]$^+$.

1-(4-Aminophenyl)-2-(*tert*-butyl)diazene 1-oxide (4g). M.p. 141—143 °C. Found (%): C, 62.07; H, 7.85; N, 21.33. $C_{10}H_{15}N_3O$. Calculated (%): C, 62.15; H, 7.82; N, 21.74. IR-(KBr), ν/cm^{-1}: 1460 (N(O)=N); 3350, 3440 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.49 (s, 9 H); 6.2 (br.s, 2 H); 6.66 (d, 1 H, *J* = 8.1 Hz); 7.85 (d, 1 H, *J* = 8.8 Hz). ^{13}C NMR (acetone-d_6), δ: 21.2, 26.3, 59.2, 117.5, 118.6, 125.1, 133.2, 142.7. MS, *m/z*: 193 [M]$^+$.

1-(2-Aminophenyl)-2-methyldiazene 1-oxide (4h). Yellow-brown oil. Found (%): C, 55.79; H, 6.09; N, 27.57. $C_7H_9N_3O$. Calculated (%): C, 55.62; H, 6.00; N, 27.80. IR (KBr), ν/cm^{-1}: 1470 (N(O)=N); 3320, 3410 (NH_2). ^{1}H NMR (acetone-d_6), δ: 3.40 (s, 3 H); 6.30 (br.s, 2 H); 6.64 (t, 1 H, *J* = 8.2 Hz); 6.93 (d, 1 H, *J* = 8.2 Hz); 7.21 (t, 1 H, *J* = 8.2 Hz); 7.96 (d, 1 H, *J* = 8.2 Hz). ^{13}C NMR (acetone-d_6), δ: 39.6, 116.4, 118.8, 125.2, 132.6, 143.5. MS, *m/z*: 151 [M]$^+$.

1-(2-Aminophenyl)-2-isopropyldiazene 1-oxide (4i). Orange-yellow oil. Found (%): C, 60.59; H, 7.13; N, 23.56. $C_9H_{13}N_3O$. Calculated (%): C, 60.32; H, 7.31; N, 23.45. IR (thin layer), ν/cm^{-1}: 1500 (N(O)=N); 3350, 3470 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.26 (d, 6 H, *J* = 6.6 Hz); 4.35 (sept, 1 H, *J* = 6.6 Hz); 6.40 (br.s, 2 H); 6.67 (dt, 1 H, *J* = 8.1 Hz, *J* = 1.5 Hz); 6.93 (dd, 1 H, *J* = 8.1 Hz, *J* = 1.5 Hz); 7.21 (dt, 1 H, *J* = 8.1 Hz, *J* = 1.5 Hz); 7.92 (dd, 1 H, *J* = 8.1 Hz, *J* = 1.5 Hz). MS, *m/z*: 179 [M]$^+$.

2-(Adamantan-1-yl)-1-(2-aminophenyl)diazene 1-oxide (4j). M.p. 122—124 °C. Found (%): C, 71.03; H, 7.51; N, 15.08. $C_{16}H_{21}N_3O$. Calculated (%): C, 70.82; H, 7.80; N, 15.49.

IR (KBr), ν/cm^{-1}: 1490 (N(O)=N); 3340, 3490 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.80 (m, 6 H); 2.22 (m, 3 H); 2.24 (m, 6 H); 6.30 (br.s, 2 H); 6.62 (dt, 1 H, J = 8.2 Hz, J = 1.5 Hz); 6.90 (dd, 1 H, J = 8.2 Hz, J = 1.5 Hz); 7.18 (dt, 1 H, J = 8.2 Hz, J = 1.5 Hz); 7.92 (dd, 1 H, J = 8.2 Hz, J = 1.5 Hz). ^{13}C NMR (acetone-d_6), δ: 30.2, 37.5, 38.5, 60.8, 116.3, 118.7, 125.2, 132.3. MS, m/z: 271 $[M]^+$.

1-(2-Aminophenyl)-2-(2,4,6-trichlorophenyl)diazene 1-oxide (4k). M.p. 127—129 °C. Found (%): C, 45.86; H, 2.52; Cl, 33.78; N, 13.41. $C_{12}H_8Cl_3N_3O$. Calculated (%): C, 45.53; H, 2.55; Cl, 33.60; N, 13.27. IR (KBr), ν/cm^{-1}: 1500 (N(O)=N); 3370, 3490 (NH_2). ^{1}H NMR (acetone-d_6), δ: 5.30 (br.s, 2 H); 6.71 (t, 1 H, J = 8.1 Hz); 7.06 (d, 1 H, J = 8.8 Hz); 7.26 (s, 2 H); 7.35 (t, 1 H, J = 8.1 Hz); 8.10 (d, 1 H, J = 8.8 Hz). MS, m/z: 315 $[M]^+$.

2-(*tert*-Butyl)-1-(4,6-dibromo-2-hydroxyaminophenyl)diazene 1-oxide (5). M.p. 128—130 °C. Found (%): C, 32.34; H, 3.55; Br, 43.37; N, 14.31. $C_{10}H_{13}Br_2N_3O_2$. Calculated (%): C, 32.72; H, 3.57; Br, 43.54; N, 14.45. IR (KBr), ν/cm^{-1}: 1480 (N(O)=N); 3380, 3420 (NHOH). ^{1}H NMR (acetone-d_6), δ: 1.46 (s, 9 H); 7.32 and 7.53 (both d, 1 H each, J = 2.2 Hz); 7.80 (br.s, 1 H); 8.20 (br.s, 1 H). MS, m/z: 365 $[M]^+$.

Ethyl 2-(2-nitrophenyl)hydrazinecarboxylate (6). M.p. 72—74 °C. IR (KBr), ν/cm^{-1}: 1530, 1340 (NO_2); 1700 (C=O); 3290 (NHNH). ^{1}H NMR (acetone-d_6), δ: 1.21 (t, 3 H, J = 6.6 Hz); 4.14 (q, 2 H, J = 6.6 Hz); 6.90 (t, 1 H, J = 8.1 Hz); 7.28 (d, 1 H, J = 8.8 Hz); 7.59 (t, 1 H, J = 8.1 Hz); 8.13 (d, 1 H, J = 8.8 Hz); 8.50 and 9.10 (both br.s, 1 H each). ^{13}C NMR (acetone-d_6), δ: 14.9, 62.1, 115.5, 118.9, 126.7, 137.0, 146.9, 157.3. MS, m/z: 225 $[M]^+$.

1-(2-Amino-4,5-dibromophenyl)-2-(*tert*-butyl)diazene 1-oxide (7b). *N*-Bromosuccinimide (0.2 g, 1.1 mmol) was added with stirring to a solution of aniline **4b** (0.3 g, 1.125 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred at 20 °C for 30 min, the solvent was evaporated, the product was extracted from the solid residue with light petroleum (hereinafter, 40—70 °C, 3×20 mL), and the solvent was evaporated. Amine **7b** was obtained in a yield of 0.302 g (77%), m.p. 102—104 °C (from hexane). Found (%): C, 34.36; H, 3.72; Br, 45.58; N, 11.76. $C_{10}H_{13}Br_2N_3O$. Calculated (%): C, 34.21; H, 3.73; Br, 45.52; N, 11.97. IR (KBr), ν/cm^{-1}: 1470 (N(O)=N); 3310, 3430 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.44 (s, 9 H); 6.57 (br.s, 2 H); 7.28 and 8.19 (both s, 1 H each). ^{13}C NMR (acetone-d_6), δ: 26.0, 59.7, 108.4, 122.5, 127.9, 129.2, 132.7 (br), 143.8. ^{14}N NMR (acetone-d_6), δ: −50.9 ($\Delta\nu_{1/2}$ = 130 Hz); −318 (br). MS, m/z: 349 $[M]^+$.

1-(2-Amino-3-bromo-5-methylphenyl)-2-(*tert*-butyl)diazene 1-oxide (7d). *N*-Bromosuccinimide (0.34 g, 1.9 mmol) was added with stirring to a solution of aniline **4d** (0.36 g, 1.74 mmol) in MeCN (7.2 mL). The reaction mixture was stirred at 20 °C for 1 h. Then the solvent was evaporated, the product was extracted from the solid residue with hot light petroleum (3×25 mL), and the solvent was evaporated. Amine **7d** was obtained in a yield of 0.45 g (91%), m.p. 125—127 °C. Found (%): C, 46.11; H, 5.57; Br, 27.84; N, 14.49. $C_{11}H_{16}BrN_3O$. Calculated (%): C, 46.17; H, 5.64; Br, 27.92; N, 14.68. IR (KBr), ν/cm^{-1}: 1500 (N(O)=N); 3330, 3470 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.49 (s, 9 H); 2.22 (s, 3 H); 6.00 (br.s, 2 H); 7.34 and 7.73 (both d, 1 H each, J = 1.5 Hz). ^{13}C NMR (acetone-d_6), δ: 20.4, 26.5, 59.9, 111.5, 125.3, 126.6, 136.3, 138.4. ^{14}N NMR (acetone-d_6), δ: −49.1 ($\Delta\nu_{1/2}$ = 200 Hz). MS, m/z: 285 $[M]^+$.

1-(2-Amino-3-bromo-5,6-dimethylphenyl)-2-(*tert*-butyl)diazene 1-oxide (7e). *N*-Bromosuccinimide (21 mg, 0.13 mmol) was added with stirring to a solution of aniline **4e** (24 mg, 0.109 mmol) in MeCN (2 mL). The reaction mixture was stirred at 20 °C for 1.5 h, the solvent was evaporated, the product was extracted from the solid residue with hot light petroleum (4×5 mL), and the solvent was evaporated. Amine **7e** was obtained in a yield of 31 mg (94%), m.p. 148—150 °C. Found (%): C, 48.16; H, 5.99; Br, 26.71; N, 13.91. $C_{12}H_{18}BrN_3O$. Calculated (%): C, 48.01; H, 6.04; Br, 26.62; N, 14.00. IR (KBr), ν/cm^{-1}: 1490 (N(O)=N); 3340, 3420 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.46 (s, 9 H); 2.04 and 2.14 (both s, 3 H each); 4.50 (br.s, 2 H); 7.26 (s, 1 H). ^{13}C NMR (acetone-d_6), δ: 14.0, 18.9, 25.9, 60.4, 107.2, 128.2, 129.7, 133.7, 136.7. ^{14}N NMR (acetone-d_6), δ: −49.8 ($\Delta\nu_{1/2}$ = 110 Hz). MS, m/z: 298 $[M]^+$.

1-(2-Amino-3,4,5-tribromophenyl)-2-(*tert*-butyl)diazene 1-oxide (8b). *N*-Bromosuccinimide (1.1 g, 6.1 mmol) was added with stirring to a solution of aniline **4b** (0.8 g, 3 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was stirred at 20 °C for 5 h and then kept without stirring for ~16 h. The solution was concentrated to dryness, the product was extracted from the solid residue with hot light petroleum (3×50 mL), and the solvent was evaporated. Amine **8b** was obtained in a yield of 1.22 g (95%), m.p. 105—106 °C. Found (%): C, 27.86; H, 2.76; Br, 55.82; N, 9.61. $C_{10}H_{12}Br_3N_3O$. Calculated (%): C, 27.94; H, 2.81; Br, 55.76; N, 9.77. IR (KBr), ν/cm^{-1}: 1470 (N(O)=N); 3290, 3470 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.48 (s, 9 H); 6.90 (br.s, 2 H); 8.29 (s, 1 H). ^{13}C NMR (acetone-d_6), δ: 26.0, 60.4, 109.0, 114.8, 128.6, 131.5, 133.4 (br), 141.6. ^{14}N NMR (acetone-d_6), δ: −51.3 ($\Delta\nu_{1/2}$ = 130 Hz). MS, m/z: 425 $[M]^+$.

1-(2-Amino-3,5-dibromophenyl)-2-methyldiazene 1-oxide (8h). Sodium acetate (1.83 g, 22.6 mmol) was added with stirring to a solution of aniline **4h** (1.64 g, 10.9 mmol) in glacial AcOH (11 mL) and then a solution of Br_2 (3.5 g, 21.8 mmol) in AcOH (5.5 mL) was added over 5 min. The reaction mixture was stirred for 5 min, poured into water (100 mL), and extracted with hexane (4×50 mL). The solvent was evaporated and the product was purified by column chromatography ($CHCl_3$ as the eluent). Amine **8h** was obtained in a yield of 1.52 g (45%), m.p. 63—65 °C. Found (%): C, 27.26; H, 2.32; Br, 51.58; N, 13.46. $C_7H_7Br_2N_3O$. Calculated (%): C, 27.21; H, 2.28; Br, 51.72; N, 13.60. IR (KBr), ν/cm^{-1}: 1470 (N(O)=N); 3350, 3440 (NH_2). ^{1}H NMR (acetone-d_6), δ: 3.43 (s, 3 H); 6.61 (br.s, 2 H); 7.74 and 8.09 (both d, 1 H each, J = 2.3 Hz). ^{13}C NMR (acetone-d_6), δ: 40.0, 106.2, 112.1, 127.6, 134.6 (br), 137.9, 140.5. ^{14}N NMR (acetone-d_6), δ: −47.9 ($\Delta\nu_{1/2}$ = 80 Hz); −314 (br). MS, m/z: 307 $[M]^+$.

1-(2-Amino-3,5-dibromophenyl)-2-isopropyldiazene 1-oxide (8i). *N*-Bromosuccinimide (0.89 g, 5 mmol) was added with stirring to a solution of aniline **4i** (0.43 g, 2.275 mmol) in MeCN (9.5 mL) and then the reaction mixture was stirred at 20 °C for 5 h. The precipitate of succinimide was filtered off and washed on a filter with a small amount of CH_2Cl_2. The filtrate was concentrated, the product was extracted from the residue with hot light petroleum, and the extract was passed through a short column with silica gel ($CHCl_3$ as the eluent). Amine **8i** was obtained in a yield of 0.73 g (92%) as an orange-yellow oil. Found (%): C, 32.18; H, 3.24; Br, 47.96; N, 12.32. $C_9H_{11}Br_2N_3O$. Calculated (%): C, 32.07; H, 3.29; Br, 47.42; N, 12.47. IR (KBr), ν/cm^{-1}: 1480 (N(O)=N); 3350, 3470 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.29 (d, 6 H, J = 7.4 Hz); 4.37

(sept, 1 H, J = 7.4 Hz); 6.63 (br.s, 2 H); 7.77 and 8.11 (both d, 1 H each, J = 2.2 Hz). ^{13}C NMR (acetone-d_6), δ: 19.8, 52.6, 127.7, 137.8. ^{14}N NMR (acetone-d_6), δ: −52.4 ($\Delta\nu_{1/2}$ = 100 Hz), −312 ($\Delta\nu_{1/2}$ = 700 Hz). MS, m/z: 335 $[M]^+$.

2-(Adamantan-1-yl)-1-(2-amino-3,5-dibromophenyl)diazene 1-oxide (8j). *N*-Bromosuccinimide (0.92 g, 5.16 mmol) was added with stirring to a solution of aniline **4j** (0.7 g, 2.58 mmol) in MeCN (10 mL) and then the reaction mixture was stirred at 20 °C for 2.5 h. The precipitate that formed was filtered off and washed on a filter with a small amount of CH_2Cl_2. The filtrate was concentrated, the product was extracted from the residue with hot light petroleum, and the extract was passed through a short column with silica gel ($CHCl_3$ as the eluent). Amine **8j** was obtained in a yield of 0.92 g (83%), m.p. 118—120 °C. Found (%): C, 44.65; H, 4.50; Br, 37.32; N, 9.69. $C_{16}H_{19}Br_2N_3O$. Calculated (%): C, 44.78; H, 4.46; Br, 37.79; N, 9.79. IR (KBr), ν/cm^{-1}: 1490 (N(O)=N); 3310, 3470 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.75 (m, 6 H); 2.10 and 2.24 (both m, 3 H each); 6.60 (br.s, 2 H); 7.76 and 8.06 (both d, 1 H each, J = 2.1 Hz). ^{14}N NMR (acetone-d_6), δ: −52.65 ($\Delta\nu_{1/2}$ = 140 Hz). MS, m/z: 427 $[M]^+$.

1-(2-Amino-3,5-dichlorophenyl)-2-(*tert*-butyl)diazene 1-oxide (9a). A 30% aqueous solution of H_2O_2 (1.6 mL) was added dropwise with stirring to a solution of aniline **4a** (1.2 g, 7 mmol) in concentrated HCl (10 mL) at 50—60 °C. Then the reaction mixture was heated for 5 min, cooled, poured into water (50 mL), and neutralized with an aqueous solution of sodium carbonate. The product was extracted with ether (3×100 mL), the extract was dried with $MgSO_4$, the solvent was concentrated, and the product was purified by column chromatography (CH_2Cl_2 as the eluent). Amine **9a** was obtained in a yield of 1.12 g (61%), m.p. 33—34 °C. Found (%): C, 45.76; H, 5.02; Cl, 27.17; N, 16.19. $C_{10}H_{13}Cl_2N_3O$. Calculated (%): C, 45.82; H, 5.00; Cl, 27.05; N, 16.03. IR (KBr), ν/cm^{-1}: 1490 (N(O)=N); 3360, 3490 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.47 (s, 9 H); 6.30 (br. s, 2 H); 7.25 and 7.95 (both d, 1 H each, J = 2.3 Hz). ^{14}N NMR (acetone-d_6), δ: −51.4 ($\Delta\nu_{1/2}$ = 120 Hz). MS, m/z: 261 $[M]^+$.

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