Organic Chemistry

Novel reaction of 1-aryl-2-bromodiazene 1-oxides with olefins. Synthesis of 1-aryl-2-(2-bromoalkyl)diazene 1-oxides

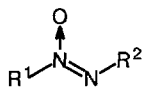
A. M. Churakov, A. Yu. Tyurin, E. L. Goncharova, S. L. Ioffe, Yu. A. Strelenko, and V. A. Tartakovsky*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328

The addition of 1-aryl-2-bromodiazene 1-oxides to olefins yields 1-aryl-2-(2-bromoalkyl)diazene 1-oxides (**4**). A radical mechanism of the reaction has been suggested. Compounds **4** decompose to give bromohydrazones of formaldehyde and aldehydes. The structural factors that affect the rate of this process are discussed.

Key words: diazene oxides, olefins, bromohydrazones; radicals, radical addition, cycloaddition.

Three approaches to the regioselective synthesis of azoxy compounds involving the formation of the R^1—N, N=N, and N—R^2 bonds, respectively, are known.



The first[1] is based on the alkylation of diazotates. The second method[2a,b] is the reaction of nitroso compounds with *N,N*-dihaloamines. The third method[3] involves the reaction of azoxy fluorides with Grignard reagents. All of these methods have some limitations and do not always make it possible to obtain the target compounds. In the present work we suggest a novel regiospecific method for the synthesis of azoxy compounds that involves the formation of the N—R^2 bond through the reaction of *N*-bromodiazene oxides (BDO) with olefins.

We prepared *N*-bromodiazene oxides for the first time[4] by the reaction of aromatic nitroso compounds with nitrogen tribromide[5] generated *in situ* by passing gaseous ammonia through a suspension of a brominating agent (*N*-bromosuccinimide (NBS) or *N,N*-dibromoisocyanurate) in an organic solvent at −60 °C. This method is similar to the synthesis of azoxy compounds by the reaction of *N,N*-dihaloamines with nitroso compounds according to Kovacic.[2b] In the present paper we describe an improved method for the synthesis of BDO. It involves the use of ammonium bromide (instead of gaseous ammonia), which substantially facilitates dosing and makes it more precise.* MeCN was chosen as the solvent, since in CH_2Cl_2 ammonium bromide is practically

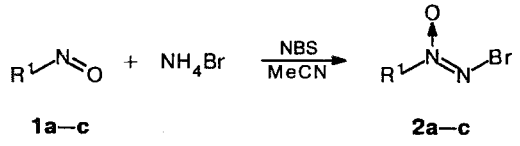
* A modification of the Kovacic method involving salts of primary amines, dibromoisocyanuric acid, and nitroso compounds has been reported previously.[6]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 917—923, May, 1995.

1066-5285/95/4405-0890 $12.50

insoluble and the rate of the reaction is much lower. The use of NH_4Br (Scheme 1), instead of gaseous ammonia, makes it possible to conduct the process at −10 to 0 °C, rather than at −60 °C.[4] The yield of BDO is nearly quantitative.

Scheme 1



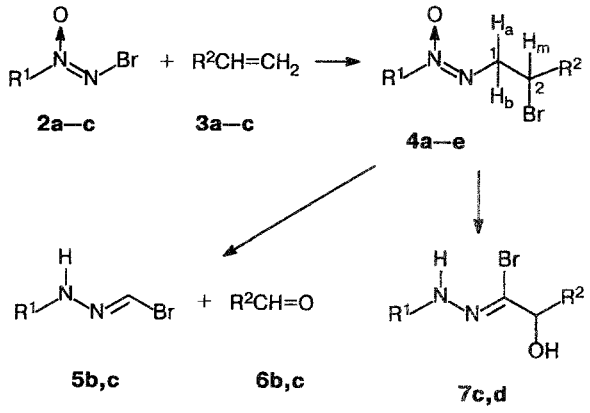
1a–c **2a–c**

R^1 = Ph (**a**); 2,4,6-$Cl_3C_6H_2$ (**b**); 2,4,6-$Br_3C_6H_2$ (**c**)

N-Bromodiazene oxides are a previously unknown class of compounds. When we studied the reactivity of BDO, we found that they regioselectively add to terminal olefins (Scheme 2) in such a fashion that the azoxy group goes to the terminal C atom and bromine adds to the substituted C atom (see the preliminary communication[7]).

The NMR spectroscopy data for compounds **4** are listed in Tables 1 and 2. The presence of the azoxy fragment was confirmed by the narrow signal at −50 to −60 ppm associated with the N atom attached to oxygen in the ^{14}N NMR spectra. The location of the Br atom was determined from the chemical shifts of the

Scheme 2



2a–c **3a–c** **4a–e**

5b,c **6b,c** **7c,d**

3, 6: $R^2 = {}^{3}CH_2{}^{4}CH_2{}^{5}CH_2{}^{6}CH_3$ (**a**); Ph (**b**); OEt (**c**)

5: R^1 = 2,4,6-$Cl_3C_6H_2$ (**b**); 2,4,6-$Br_3C_6H_2$ (**c**)

4, 7: R^1 = Ph, R^2 = Bu (**a**);

R^1 = 2,4,6-$Cl_3C_6H_2$, R^2 = Bu (**b**);

R^1 = 2,4,6-$Cl_3C_6H_2$, R^2 = Ph (**c**);

R^1 = 2,4,6-$Br_3C_6H_2$, R^2 = Ph (**d**);

R^1 = 2,4,6-$Br_3C_6H_2$, R^2 = OEt (**e**)

signals for the C(1) and C(2) atoms in the ^{13}C NMR spectra and from the multiplicity of these signals in the spectra recorded without ^1H—^{13}C decoupling. Com-

Table 1. ^{13}C and ^{14}N NMR spectroscopy data for compounds **4**

Compound	^{13}C NMR, δ										^{14}N NMR, δ ($\Delta\nu_{1/2}$/Hz)
	R^1				C(1)	C(2)	R^2				
	C—N	C_o	C_m	C_p			C(3) or C—CH	C(4) or C_o	C(5) or C_m	C(6) or C_p	
4a	147.00 (br)	122.16	128.80	131.53	59.47	52.16	36.90	28.70	22.12	13.85	−50 (150)
4b	143.00 (br)	129.33	128.72	135.85	59.48	50.54	36.49	29.72	21.86	13.76	−57 (300)
4c	143.17 (br)	129.20	128.62	135.77	59.60	48.89	139.43	127.56	128.73	128.77	−58.9 (290)
4d	146.70 (br)	117.24	134.92	123.77	59.72	48.94	139.57	127.68	128.80	128.84	−52 (250)

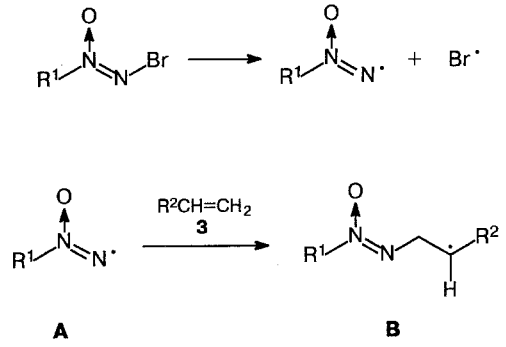
Table 2. ^1H NMR spectroscopy data for compounds **4**

Compound	δ (*J*/Hz)									
	R^1			$H_aC(1)$	$H_bC(1)$	$H_mC(2)$	R^2			
	H_o	H_m	H_p				HC(3)	HC(4) or HC_o	HC(5) or HC_m	HC(6) or HC_p
4a	8.16 d	7.44 t	7.49 t	4.05 ($^3J_{a,m}$ = 6.0)	4.10 ($^2J_{a,b}$ = −19.2)	4.43 tt ($^3J_{b,m}$ = 6.4)	1.98 dt	1.4—1.55 m		0.92 t
4b		7.42		4.11	4.14	4.40 tt	1.95 dt	1.3—1.45 m		0.92 t
4c		7.33		4.43	4.48	5.44		7.45	7.28—7.35 m	
4d		7.71		4.42 ($^3J_{a,m}$ = 6.8)	4.47 ($^2J_{a,b}$ = −18.6)	5.46 ($^3J_{b,m}$ = 7.8)		7.47 dd	7.31—7.34 m	

pounds **4** cannot be isolated in the analytically pure state due to their low stability, but their structure was unambiguously determined by spectral methods. The structure of diazene oxides **4** was convincingly confirmed by the conversion of compound **4a** into olefin **13** (see below), whose structure rules out the alternative position of the bromo and azoxy substituents in molecule **4**.

BDO react with electron-enriched olefins at higher rates. The reaction with ethyl vinyl ether is completed within 30 min even at −15 °C. The completion of the reaction with styrene requires 2 h at 40 °C, and the reaction with freshly distilled 1-hexene virtually does not occur under the same conditions. However, if 1-hexene contains 0.05 g-equiv. L^{-1} of peroxides, the complete conversion of BDO is achieved over a period of 8 h at 40 °C (or 2 days at 24 °C). We were not able to react allyl chloride with BDO. The reaction of BDO with styrene is accelerated by UV irradiation; however, we did not develop this procedure due to the possibility of the migration of oxygen in the diazene oxide fragment. Based on the above data, a radical mechanism of the reaction of BDO with alkenes can be suggested. The reaction begins with the interaction between diazene oxide radical **A** and an olefin (Scheme 3).

Scheme 3



The reactivities of olefins correlate with the ability of the substituent R^2 to stabilize the resulting radical **B**. The latter can either react with Br˙ or abstract the Br atom from another BDO molecule and thus continue the chain process. The former route is more likely for the reactions of BDO with styrene or ethyl vinyl ether. In this case, radical **A** probably exists as a tight pair with the Br˙ radical and reacts with an olefin in a cage. The second route is more likely for the reaction with 1-hexene, which does not occur without a radical initiator. It should be noted that there are no reliable data in the literature concerning the existence of type **A** radicals. However, they have been suggested as intermediates in some processes, for example, in the reaction of azoxy fluorides with Grignard reagents[3] and in the thermal decomposition of some azoxy compounds.[8]

It is unlikely that BDO react with olefins by an ionic mechanism, since in this case, the process should begin with the attack of a positively charged Br atom on the terminal C atom of the olefin, which would have resulted in the opposite arrangement of the substituents in the products.

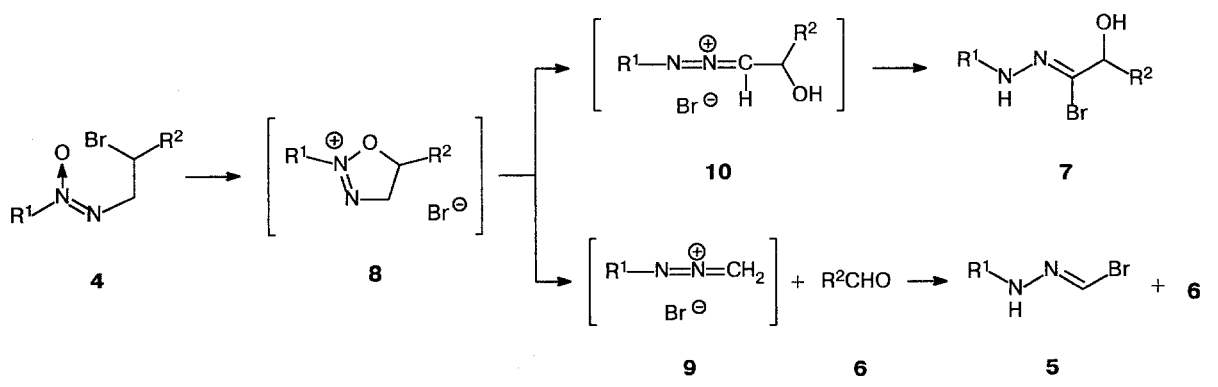
Compounds **4c,d** (R^2 = Ph) contain an active Br atom and a nucleophilic site, the *N*-oxide O atom, which determines the pathway of decomposition of these diazene oxides.

Compounds **4c,d** decompose entirely on silica gel over a period of 1 h at 20 °C to give benzaldehyde and bromohydrazones **5b,c** (see Scheme 2). The yields of bromohydrazones are not quantitative, since they also slowly decompose on silica gel.

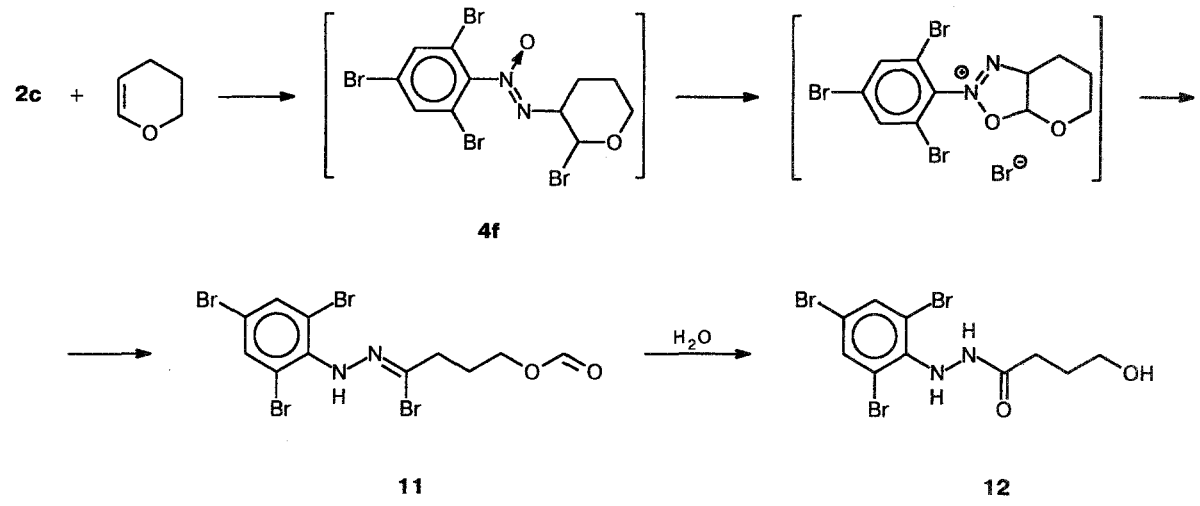
In nonpolar organic solvents (benzene, chloroform), diazene oxides **4c,d** decompose over a period of several days to give bromohydrazones **5b,c** and **7c,d**. In dilute solutions the yields of products **7** vary from 6 to 18 %, whereas in a saturated $CHCl_3$ solution, this reaction route predominates, and the yield of hydrazone **7c** can be as high as 58 %. This behavior of compounds **4** can be explained by the formation of intermediate cation **8** (Scheme 4), which can decompose to give the stable cation **9** and benzaldehyde. The second reaction pathway is probably cleavage of the N—O bond of the ring in intermediate **8** to give the stable cation **10**. In turn, cations **9** and **10** are converted into the corresponding hydrazones **5** and **7**.

In conformity with the scheme presented, the stability of compounds **4** should depend on the nucleophilic-

Scheme 4



Scheme 5



4f

11 **12**

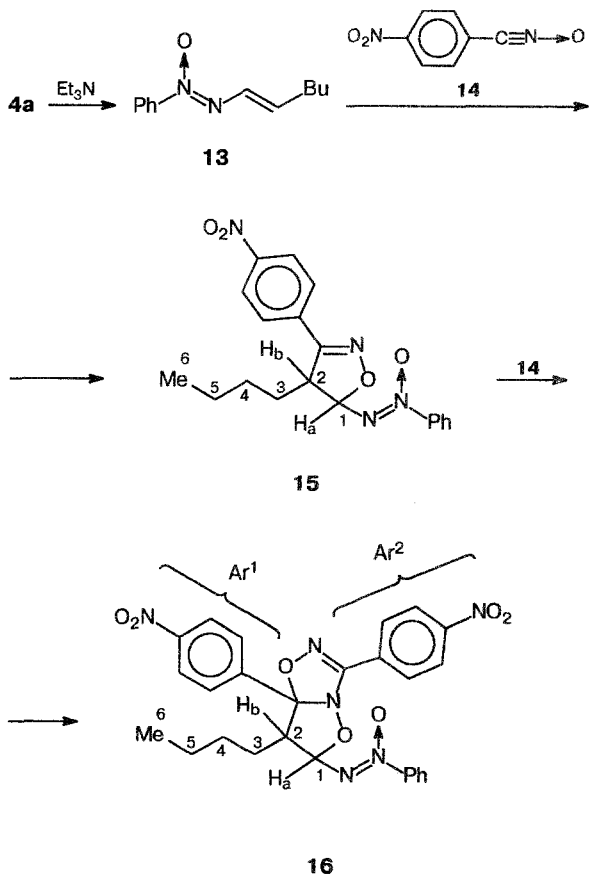
ity of the O atom of the azoxy group (which is determined by the substituent R^1) and on the mobility of the Br atom (which is governed by the substituent R^2). This accounts for the fact that compound **4e** (R^2 = OEt) is so unstable that it cannot be isolated. The reaction of BDO **2c** with ethyl vinyl ether yields bromohydrazone **5c** and ethyl formate resulting from decomposition of **4e**. Compound **4f** formed in the reaction of **2c** with dihydropyran is also unstable. Due to structural features, the bromohydrazone moiety and the C=O group formed in the decomposition of the intermediate compound **4f** remain within one molecule **11** (Scheme 5). The structure of compound **11** was confirmed by spectroscopy data and by its hydrolysis to yield compound **12**.

The reaction of BDO **2a** with styrene affords a complex mixture of products, from which benzaldehyde and 1,2-dibromo-1-phenylethane were isolated. This reaction course must be due to the low rate of decomposition of the intermediate, *viz.*, cyclic salt **8** (R^1 = R^2 = Ph) (see Scheme 4). The anion of this salt has time to react with the starting BDO to yield bromine, which, in turn, adds to styrene. In the case of the reaction of ethyl vinyl ether and dihydropyran with compound **2c**, the intermediate salt **8** apparently decomposes much more rapidly than it could react with BDO, and therefore, bromine is not liberated.

As was noted above, to confirm the structure of compound **4a**, it was converted into olefin **13** by treatment with Et_3N. The isomers of **13** (the *E*/*Z* ratio was ~1 : 1) were assigned by comparing the vicinal spin coupling constants of the olefinic protons.[9] Compound **13** is a nondistillable oil. Its structure was determined by spectral methods and also by its cycloaddition to *p*-nitrobenzonitrile *N*-oxide (**14**) (Scheme 6).

Along with the primary adduct **15** (a mixture of isomers), the reaction affords compounds **16*** (also as a mixture of isomers). Products **15** and **16** were characterized by spectral methods and elemental analysis. The assignment of isomers was based on a comparison of vicinal spin coupling constants of protons. The individual *trans*-isomer of **15** (isolated by column chromatography) was converted into individual *trans*-**16** by

Scheme 6



13 **15** **16**

* Previously[10] the formation of adducts of nitrile oxides with isoxazolines has been described.

reaction with nitrile oxide **14**. By comparing the spectrum of *trans*-**16** with the spectrum of a mixture of isomers of **16** (that we could not separate by chromatography), we assigned some signals to the *cis*-isomer of **16**.

Experimental

The following compounds were prepared according to literature procedures: PhNO,[11] 2,4,6-$Cl_3C_6H_2NO$,[12] and 2,4,6-$Br_3C_6H_2NO$.[12] The ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13, 75.5, 21.5, and 30.42 MHz, respectively); the chemical shifts were referred to tetramethylsilane (^1H, ^{13}C) or $MeNO_2$ (^{14}N, ^{15}N, an external standard). To observe ^{15}N signals, the INEPT and SPT procedures were used. The signals in the ^1H and ^{13}C NMR spectra were assigned using $^1H—^{13}C$ and $^1H—^1H$ correlations, the ^{13}C NMR spectra recorded without proton decoupling, and the accumulation of ^{13}C signals with selective proton decoupling. The IR spectra were recorded on a UR-20 spectrometer (in thin films between NaCl glasses for liquids or for samples pressed with KBr for solids). Mass spectra were obtained on a Varian MAT CH-6 instrument.

Synthesis of 1-aryl-2-bromodiazene 1-oxides (2) (general procedure). An arylnitroso compound (50 mmol) and NBS (240 mmol) were suspended in a mixture of 100 mL of CH_2Cl_2 and 100 mL of MeCN. Finely powdered NH_4Br (60 mmol) was added with intense stirring and cooling to −10 °C, and the mixture was kept for 1 h at −10 to 0 °C and concentrated under reduced pressure (at a temperature of the bath of <40 °C). The product was extracted with pentane, and the solvents were evaporated *in vacuo*.

1-Phenyl-2-bromodiazene 1-oxide (2a). Yield 95 %, m.p. 46—47 °C (from pentane). Found (%): C, 35.71; H, 2.45; N, 14.02; Br, 39.98. $C_6H_5N_2OBr$. Calculated (%): C, 35.85; H, 2.51; N, 13.94; Br, 39.75. MS, *m/z*: 200 $[M]^+$ (for the ^{79}Br isotope). IR, ν/cm^{-1}: 1472 (N(O)N). ^1H NMR ($CDCl_3$), δ: 7.47 (H_m); 7.56 (H_p); 8.05 (H_o). ^{13}C NMR, δ: 122.51 (C_o); 129.21 (C_m); 132.48 (C_p); 145.13 (C—N). ^{14}N NMR, δ: −38.3 (NO, $\Delta\nu_{1/2}$ = 46 Hz); −62 (NBr, $\Delta\nu_{1/2}$ > 400 Hz).

1-(2,4,6-Trichlorophenyl)-2-bromodiazene 1-oxide (2b). Yield 95 %, m.p. 76—77 °C (from pentane). Found (%): C, 23.78; H, 0.51; N, 9.45; Cl + Br, 61.35. $C_6H_2N_2OCl_3Br$. Calculated (%): C, 23.68; H, 0.66; N, 9.20; Cl + Br, 61.2. MS, *m/z*: 302 $[M]^+$ (for the ^{35}Cl and ^{79}Br isotopes). IR, ν/cm^{-1}: 1446 (N(O)N). ^1H NMR ($CDCl_3$), δ: 7.36 (H_m). ^{13}C NMR, δ: 126.95 (C_m); 129.69 (C_o); 137.23 (C_p); 140.45 (C—N). ^{14}N NMR, δ: −41.9 ($\Delta\nu_{1/2}$ = 80 Hz).

1-(2,4,6-Tribromophenyl)-2-bromodiazene 1-oxide (2c). Yield 95 %, m.p. 95—96 °C. Found (%): C, 16.57; H, 0.49; N, 6.75; Br, 73.33. $C_6H_2N_2Br_4O$. Calculated (%): C, 16.44; H, 0.46; N, 6.39; Br, 73.06. MS, *m/z*: 434 $[M]^+$ (for the ^{79}Br isotope). IR, ν/cm^{-1}: 1465 (N(O)N). ^1H NMR ($CDCl_3$), δ: 7.84 (2 H, $^4J_{H,H}$ = 1.8 Hz (determined from the ^{13}C satellites of the main signal)). ^{13}C NMR, δ: 117.87 (C_o); 125.84 (C_p); 135.81 (C_m); 144.75 (C—N). ^{14}N NMR, δ: −41.9 ($\Delta\nu_{1/2}$ = 56 Hz).

1-Phenyl-2-(2-bromohexyl)diazene 1-oxide (4a). 1-Hexene (15 mL, 120 mmol) containing 0.05 g-equiv. L^{-1} of peroxides was added to a solution of diazene oxide **2a** (6 g, 30 mmol) in 18 mL of CH_2Cl_2, and the mixture was kept for 8 h at 40 °C and concentrated in a vacuum of an oil pump. The residue was purified by column chromatography (silica gel, hexane—chloroform, 2 : 1) to give 5.1 g of compound **4a** as an oil (yield 60 %). MS, *m/z*: 284 $[M]^+$ (for the ^{79}Br isotope). IR, ν/cm^{-1}: 1488 (N(O)N).

1-(2,4,6-Trichlorophenyl)-2-(2-bromohexyl)diazene 1-oxide (4b) was prepared similarly to **4a** from diazene oxide **2b** and hexene, yield 63 %, an oil. MS, *m/z*: 386 $[M]^+$(for the ^{35}Cl and ^{79}Br isotopes). IR, ν/cm^{-1}: 1480 (N(O)N).

1-(2,4,6-Trichlorophenyl)-2-(2-bromo-2-phenylethyl)diazene 1-oxide (4c). Freshly distilled styrene (1.3 mL, 10.8 mmol) was added to a solution of 1-(2,4,6-trichlorophenyl)-2-bromodiazene 1-oxide (**2b**) (0.83 g, 2.7 mmol) in 1 mL of CH_2Cl_2, and the mixture was kept for 1 h at 40 °C and concentrated in a vacuum of an oil pump. The solid residue of **4c** was washed with pentane and dried *in vacuo* to give 0.93 g of compound **4c** (yield 81 %), m.p. 107—108 °C. Found (%): C, 41.43; H, 2.84; N, 6.30; Cl + Br, 45.16. $C_{14}H_{10}N_2Cl_3BrO$. Calculated (%): C, 41.13; H, 2.45; N, 6.85; Cl + Br, 45.65. MS, *m/z*: 406 $[M]^+$ (for the ^{35}Cl and ^{79}Br isotopes). IR, ν/cm^{-1}: 1500 (N(O)N).

1-(2,4,6-Tribromophenyl)-2-(2-bromo-2-phenylethyl)diazene 1-oxide (4d) was prepared from 1-(2,4,6-tribromophenyl)-2-bromodiazene 1-oxide **2c** and styrene similarly to compound **4c**, but without a solvent. Yield 97 %, m.p. 113—117 °C (dec.). Found (%): C, 31.42; H, 1.57; N, 5.60; Br, 59.32. $C_{14}H_{10}N_2Br_4O$. Calculated (%): C, 31.00; H, 1.85; N, 5.16; Br, 59.04. MS, *m/z*: 538 $[M]^+$ (for the ^{79}Br isotope). IR, ν/cm^{-1}: 1475 (N(O)N).

Reaction of 1-phenyl-2-bromodiazene 1-oxide (2a) with styrene. A mixture of diazene oxide **2a** (0.5 g, 2.5 mmol) and styrene (0.9 mL, 7.5 mmol) was kept for 1 h at 45 °C. The yields of the products determined by ^1H NMR spectroscopy with an internal standard (hexamethyldisiloxane) were the following: benzaldehyde, 36 %; 1,2-dibromo-1-phenylethane, 29 %. The structures of the products were confirmed by comparison with authentic samples.

Reaction of 1-(2,4,6-tribromophenyl)-2-bromodiazene 1-oxide (2c) with ethyl vinyl ether. Diazene oxide **2c** (0.62 g, 1.4 mmol) was dissolved in 2 mL of CH_2Cl_2, and the solution was cooled to −50 °C. Ethyl vinyl ether (0.3 mL, 2.8 mmol) was added with stirring, and the mixture was kept for 30 min at −15 °C. The yields of the products determined by ^1H NMR spectroscopic analysis of the reaction mixture were the following: 2,4,6-tribromophenylhydrazone of formyl bromide **(5c)**, 89 %; ethyl formate **(6c)**, 71 %. Compound **5c** was isolated by column chromatography (silica gel, chloroform—hexane, 1 : 2), m.p. 122—124 °C. Found (%): C, 19.50; H, 0.75; N, 6.29; Br, 73.56. $C_7H_4N_2Br_4$. Calculated (%): C, 19.27; H, 0.92; N, 6.42; Br, 73.39. MS, *m/z*: 432 $[M]^+$ (for the ^{79}Br isotope). IR, ν/cm^{-1}: 3260 (NH). ^1H NMR ($CDCl_3$), δ: 7.26 (s, 1 H, CH=); 7.72 (s, 2 H, ArH); 8.0 (br.s, 1 H, NH). ^{13}C NMR, δ: 107.62 (=CH, $^1J_{1H-13C}$ = 246 Hz, $^3J_{1H-13C}$ = 8.7 Hz); 117.23 (C_o, $^3J_{1H-13C}$ = 4 Hz); 117.61 (C_p, $^2J_{1H-13C}$ = 4.3 Hz); 135.67 (C_m, $^1J_{1H-13C}$ = 173.8 Hz, $^3J_{1H-13C}$ = 6.4 Hz); 138.80 (C—N, Ar). ^{14}N NMR, δ: −51 (C=N, $\Delta\nu_{1/2}$ = 400 Hz); −241 (NH, $\Delta\nu_{1/2}$ = 500 Hz).

Transformation of 1-(2,4,6-trichlorophenyl)-2-(2-bromo-2-phenylethyl)diazene 1-oxide (4c) on silica gel. Diazene oxide **4c** (1.51 g, 3.7 mmol) was dissolved in 30 mL of CH_2Cl_2, and silica gel (40 g) was added to the resulting solution. The solvent was evaporated *in vacuo*, the residue was kept for 1 h, the products of decomposition were washed away from the silica gel with dichloromethane, and the solvent was evaporated. Benzaldehyde (70 %, according to the ^1H NMR spectrum) was recondensed from the residue into a cooled trap under reduced pressure (0.05 Torr). Column chromatography of the residue (silica gel, chloroform—hexane, 1 : 2) gave 0.44 g of 2,4,6-trichlorophenylhydrazone of formyl bromide

(5b) (yield 40 %), m.p. 89—90 °C. Found (%): C, 27.90; H, 1.45; N, 9.29; Cl + Br, 61.86. $C_7H_4N_2Cl_3Br$. Calculated (%): C, 27.77; H, 1.32; N, 9.26; Cl + Br, 61.65. MS, *m/z*: 300 $[M]^+$ (for the ^{35}C and ^{79}Br isotopes). IR, ν/cm^{-1}: 3290 (NH). ^1H NMR ($CDCl_3$), δ: 7.23 (d, 1 H, =CH, ^4J = 1.2 Hz); 7.32 (s, 2 H, ArH); 8.0 (br.s, NH). ^{13}C NMR, δ: 107.39 (=CH, $^1J_{^1H-^{13}C}$ = 246.5 Hz); 127.15 (C_o); 128.89 (C_m); 129.18 (C_p); 135.71 (C—N, Ar). ^{14}N NMR, δ: −51 (C=N, $\Delta\nu_{1/2}$ = 400 Hz); −245 (NH, $\Delta\nu_{1/2}$ = 800 Hz). ^{15}N NMR (INEPT), δ: −246.85 (NH, $^1J_{^1H-^{15}N}$ = 88.1 Hz, $^3J_{^1H-^{15}N}$ = 7.0 Hz).

Transformation of 1-(2,4,6-trichlorophenyl)-2-(2-bromo-2-phenylethyl)diazene 1-oxide (4c) in solution. Diazene oxide **4c** (0.64 g, 1.6 mmol) was dissolved in 1.8 mL of $CHCl_3$, and the solution was kept for 6 days at 24 °C and concentrated. According to the ^1H NMR spectrum, the yield of benzaldehyde amounted to 35 %, and the yield of **5b** was 31 %. Column chromatography (silica gel, chloroform—hexane, 1 : 2) gave 0.38 g of 2,4,6-trichlorophenylhydrazone of 2-hydroxy-2-phenylacetyl bromide (**7c**) (yield 58 %), m.p. 112—114 °C. Found (%): C, 41.10; H, 2.22; N, 6.71; Cl + Br, 45.78. $C_{14}H_{10}N_2Cl_3BrO$. Calculated (%): C, 41.13; H, 2.45; N, 6.85; Cl + Br, 45.65. MS, *m/z*: 406 $[M]^+$ (for the ^{35}Cl and ^{79}Br isotopes). IR, ν/cm^{-1}: 3300 (NH). ^1H NMR ($CDCl_3$), δ: 3.40 (br.d, 1 H, OH, ^3J = 4.0 Hz); 5.49 (d, 1 H, CH); 7.32 (s, 2 H, ArH); 7.33—7.43 (m, 5 H, Ph); 7.9 (br.s, 1 H, NH). ^{13}C NMR, δ: 77.63 (HCOH); 126.86 (C_o, Ph); 126.97 (C_o, Ar and =CBr); 128.55 (C_m and C_p in Ph); 128.85 (C_p, Ar); 128.94 (C_m, Ar); 135.62 (C—CH in Ph); 138.72 (C—NH in Ar). ^{15}N NMR (INEPT), δ: −249.40 (NH, $^1J_{^1H-^{15}N}$ = 89 Hz).

Transformation of 1-(2,4,6-tribromophenyl)-2-(2-bromo-2-phenylethyl)diazene 1-oxide (4d) on silica gel. Diazene oxide **4d** (2 g, 3.7 mmol) was dissolved in 30 mL of CH_2Cl_2, and silica gel (40 g) was added to the resulting solution. The solvent was evaporated *in vacuo*, the residue was kept for 1 h, the products of decomposition were washed away from the silica gel with dichloromethane, and the solvent was evaporated. Benzaldehyde (70 %, according to the ^1H NMR spectrum) was recondensed from the residue into a cooled trap under reduced pressure (0.05 Torr). Column chromatography of the residue (silica gel, chloroform—hexane, 1 : 2) gave 1.04 g of compound **5c** (yield 65 %).

Transformation of 1-(2,4,6-tribromophenyl)-2-(2-bromo-2-phenylethyl)diazene 1-oxide (4d) in a $CHCl_3$ solution. The reaction was carried out similarly to the reaction of compound **4c**; according to the ^1H NMR spectrum, the yield of compound **5c** was 27 %, the yield of **6b** was 30 %, and that of **7d** was 55 %. The transformation of diazene oxide **4d** in a dilute $CHCl_3$ solution (0.15 mol L^{-1}) gave **5c**, **6b**, and **7d** in 70 %, 51 %, and 8.2 % yields, respectively (according to ^1H NMR).

2,4,6-Tribromophenylhydrazone of 2-hydroxy-2-phenylacetyl bromide (7d). M.p. 127—128 °C. Found (%): C, 31.20; H, 1.79; N, 5.35; Br, 58.88. $C_{14}H_{10}N_2Br_4O$. Calculated (%): C, 31.00; H, 1.85; N, 5.16; Br, 59.04. MS, *m/z*: 538 $[M]^+$ (for the ^{79}Br isotope). IR, ν/cm^{-1}: 3280 (NH). ^1H NMR ($CDCl_3$), δ: 3.4 (br.d, 1 H, OH); 5.52 (d, 1 H, CH); 7.3—7.5 (m, 5 H, Ph); 7.70 (s, 2 H, H_m, Ar); 7.9 (br.s, NH). ^{13}C NMR, δ: 77.80 (CH, $^1J_{^1H-^{13}C}$ = 149.7 Hz); 115.87 (C_o, Ar); 116.71 (C_p, Ar, $^2J_{^1H-^{13}C}$ = 4.5 Hz); 126.70 (CBr); 126.95 (C_o, Ph); 128.56 (C_p, Ph); 128.59 (C_m, Ph); 135.31 (C_m, Ar); 138.10 (C—NH in Ar); 138.82 (C—CH in Ph). ^{15}N NMR (INEPT), δ: −242.70 (NH, $^1J_{^1H-^{15}N}$ = 88 Hz).

2,4,6-Tribromophenylhydrazone of 4-formyloxybutanoyl bromide (11). 1-(2,4,6-Tribromophenyl)-2-bromodiazene 1-oxide **(2c)** (1 g, 2.28 mmol) was dissolved in 2 mL of CH_2Cl_2, and at −30 °C, 3,4-dihydro-2*H*-pyran (2.3 mL, 27.6 mmol) was added. The mixture was kept for 45 min at 0 °C and concentrated *in vacuo*, and the residual oil was extracted with pentane (3×45 mL). Evaporation of pentane in a vacuum of an oil pump gave 1.15 g of compound **11** (yield 96 %) as an oil. MS, *m/z*: 518 $[M]^+$ (for the ^{79}Br isotope). IR, ν/cm^{-1}: 3285 (NH). ^1H NMR ($CDCl_3$), δ: 2.10 (quint, 2 H, CCH_2C); 2.85 (t, 2 H, $BrCCH_2$, ^3J = 7.2 Hz); 4.25 (t, 2 H, OCH_2, ^3J = 6.8 Hz); 7.66 (s, 2 H, ArH); 7.8 (br.s, 1 H, NH); 8.05 (s, 1 H, CHO). ^{13}C NMR, δ: 25.97 ($CH_2CH_2CH_2$); 38.10 (CH_2C=); 62.40 (CH_2O); 115.9 (C_o); 116.28 (C_p); 123.30 (BrC=N); 135.10 (C_m); 138.50 (C—N from Ar); 160.80 (CHO). ^{15}N NMR (INEPT), δ: −241.12 (NH, $^1J_{^1H-^{15}N}$ = 86 Hz).

2,4,6-Tribromophenylhydrazide of 4-hydroxybutanoic acid (12). Hydrazone **11** (0.5 g, 0.96 mmol) was dissolved in a mixture of 40 mL of acetone and 20 mL of water, the solution was kept for 24 h at 20 °C, and the acetone was evaporated *in vacuo* (20 Torr) at a temperature of the bath of 30 °C. The precipitate was filtered off. Column chromatography (silica gel, chloroform followed by ethyl acetate) gave 0.21 g of compound **12** (yield 51 %), m.p. 93—95 °C. Found (%): C, 27.65; H, 2.50; N, 6.65; Br, 55.71. $C_{10}H_{11}N_2O_2Br_3$. Calculated (%): C, 27.82; H, 2.57; N, 6.50; Br, 55.63. MS, *m/z*: 428 $[M]^+$ (for the ^{79}Br isotope). IR, ν/cm^{-1}: 1662 (C=O); 3250 (NH); 3465 (OH). ^1H NMR (acetone-d_6), δ: 1.72—1.82 (m, 2 H, $CH_2CH_2CH_2$); 2.32 (t, 2 H, CH_2C=O); 2.9 (v.br.s, 1 H, OH); 3.54 (t, 2 H, CH_2OH); 6.9 and 9.3 (br, 2 H, NH); 7.69 (s, 2 H, Ar). ^{13}C NMR, δ: 29.09 (CH_2C=O); 30.73 ($CH_2CH_2CH_2$); 61.91 (CH_2OH); 114.57 (C_p); 115.08 (C_o); 135.67 (C_m); 144.31 (C—NH, Ar); 172.93 (C=O). ^{15}N NMR (INEPT), δ: −242.71 (NH, $^1J_{^1H-^{15}N}$ = 103 Hz).

1-Phenyl-2-(1-hexenyl)diazene 1-oxide (13). Triethylamine (2.5 mL, 18 mmol) was added to a stirred solution of diazene oxide **4a** (3.4 g, 12 mmol) in 4 mL of CH_2Cl_2. After 30 min the reaction mixture was diluted with water (10 mL), and an excess of triethylamine was neutralized with 5 % HCl to pH 7. The organic layer was separated, washed with water, dried with $MgSO_4$, and concentrated to give 2.4 g of compound **13** (yield 98 %), an oil. Found (%): C, 70.84; H, 7.72; N, 13.81. $C_{12}H_{16}N_2O$. Calculated (%): C, 70.59; H, 7.84; N, 13.73. MS, *m/z*: 204 $[M]^+$. IR, ν/cm^{-1}: 1472 (N(O)N); 1560 (C=C). ^1H NMR ($CDCl_3$), δ: 0.93 (t, *E*, *Z*, HC(6)); 1.35—1.42 (m, *E*, *Z*, HC(5)); 1.45—1.51 (m, *E*, *Z*, HC(4)); 2.33 (dtt, *E*, HC(3)); 2.61 (dtt, *Z*, HC(3)); 5.94 (dtt, *Z*, HC(2), ^3J = 8.0 Hz); 6.60 (dtt, *E*, HC(2), ^3J = 7.75 Hz); 7.44—7.48 (m, *E*, *Z*, H_m and H_p); 7.78 (dt, *Z*, HC(1), ^3J = 8.2 Hz); 7.91 (dt, *E*, HC(1), ^3J = 13.7 Hz); 8.20 (d, *E*, *Z*, H_o). ^{13}C NMR, δ: 13.86, 13.88 (*E*, *Z*, C(6)); 22.31, 22.36 (*E*, *Z*, C(5)); 27.32, 30.97, 31.07, 31.36 (*E*, *Z*, C(3),C(4)); 122.1, 122.2 (*E*, *Z*, C_o, R^1); 128.7 (*E*, *Z*, C_m, R^1); 131.29 (*Z*, C(1)); 131.36, 131.43 (*E*, *Z*, C_p, R^1); 133.86 (*E*, C(1)); 138.05 (*Z*, C(2)); 140.41 (*E*, C(2)); 146.8, 147.0 (br, *E*, *Z*, C—N, R^1). ^{14}N NMR for both isomers, δ: −65 (N(O)=N, $\Delta\nu_{1/2}$ = 130 Hz).

Cycloaddition of 4-nitrophenylnitrile oxide (14) to diazene oxide 13. A solution of nitrile oxide **14** (1.48 g, 9 mmol) in 45 mL of CH_2Cl_2 was added to a solution of compound **13** (0.4 g, 2 mmol) in 1 mL of CH_2Cl_2 in three equal portions at intervals of 2.5 h. The reaction mixture was kept for an additional 17 h at 20 °C, the solvent was evaporated, the residual oil was diluted with $CHCl_3$, the precipitate was filtered off, and the filtrate was evaporated. According to the ^1H NMR spectrum, the yield of *cis*-**15** was 10—12 %, the yield of *trans*-**15** was 15—17 %, and that of *cis,trans*-**16** was

22—25 %. The products were separated by column chromatography (silica gel, chloroform—hexane, 1 : 2).

The yield of *cis*-**15** was 70 mg, m.p. 137—139 °C. Found (%): C, 61.87; H, 5.44; N, 15.00. $C_{19}H_{20}N_4O_4$. Calculated (%): C, 61.95; H, 5.47; N, 15.21. MS, *m/z*: 368 $[M]^+$. IR, ν/cm^{-1}: 1350, 1528 (NO_2); 1490 (N(O)N). ^1H NMR (DMSO-d_6), δ: 0.60 (t, 3 H, CH_3); 1.04 (m, 2 H, C(5)H_2); 1.23 (m, 2 H, C(4)H_2); 1.55 (m, 2 H, C(3)H_2); 4.55 (t, 1 H, H_b, ^3J = 8.0 Hz); 6.54 (d, 1 H, H_a, $^3J_{H_a,H_b}$ = 9.3 Hz); 7.66 (t, 2 H, H_m, Ph); 7.75 (t, 1 H, H_p, Ph); 8.07 (d, 2 H, H_o, Ar); 8.15 (d, 2 H, H_o, Ph); 8.29 (d, 2 H, H_m, Ar). ^{13}C NMR, δ: 13.35 (C(6)); 22.03 (C(5)); 25.21 (C(4)); 28.56 (C(3)); 49.62 (CH_b); 95.14 (CH_a); 121.75 (C_o, Ph); 124.13 (C_m, Ph); 128.21 (C_o, Ar); 129.53 (C_m, Ar); 132.97 (C_p, Ph); 134.71 (C=N); 146.02 (C—CN, Ar); 148.28 (C—NO); 159.53 (C_p, Ar). ^{14}N NMR, δ: −20 (NO_2, $\Delta\nu_{1/2}$ > 1000 Hz); −55 (N(O)=N, $\Delta\nu_{1/2}$ > 1000 Hz).

The yield of *trans*-**15** was 0.15 g, m.p. 124—125 °C. Found (%): C, 61.82; H, 5.43; N, 14.95. $C_{19}H_{20}N_4O_4$. Calculated (%): C, 61.95; H, 5.47; N, 15.21. MS, *m/z*: 368 $[M]^+$. IR, ν/cm^{-1}: 1347, 1520 (NO_2); 1490 (N(O)N). ^1H NMR (DMSO-d_6), δ: 0.88 (t, 3 H, CH_3); 1.27—1.50 (m, 4 H, C(4)H_2, C(5)H_2); 1.65 and 1.78 (mm, 2 H, C(3)H_2); 3.94 (ddd, 1 H, H_b, ^3J = 6.1 and 1.5 Hz); 6.28 (d, 1 H, H_a, $^3J_{H_a,H_b}$ = 2.2 Hz); 7.58 (t, 2 H, H_m, Ph); 7.68 (t, 1 H, H_p, Ph); 8.03 (d, 2 H, H_o, Ar); 8.13 (d, 2 H, H_o, Ph); 8.29 (d, 2 H, H_m, Ar). ^{13}C NMR, δ: 13.85 (C(6)); 21.99 (C(5)); 27.88 (C(4)); 28.94 (C(3)); 51.86 (CH_b); 96.56 (CH_a); 121.88 (C_o, Ph); 124.05 (C_m, Ph); 128.43 (C_o, Ar); 129.21 (C_m, Ar); 132.59 (C_p, Ph); 134.06 (C=N); 146.33 (C—C=N); 148.40 (C—NO); 160.03 (C_p, Ar). ^{14}N NMR, δ: −14 (NO_2, $\Delta\nu_{1/2}$ = 750 Hz); −50 (N(O)=N, $\Delta\nu_{1/2}$ = 500 Hz).

Cycloaddition of 4-nitrophenylnitrile oxide to *trans*-15. Nitrile oxide **14** (0.5 g, 3.05 mmol) in 0.7 mL of CH_2Cl_2 was added to a solution of *trans*-**15** (60 mg, 0.16 mmol) in 2 mL of CH_2Cl_2 and 0.4 mL of MeCN. After 2 days the solvent was evaporated. Column chromatography (silica gel, chloroform—hexane, 1 : 2) gave 70 mg (83 %) of *trans*-**16**, m.p. 129—131 °C. Found (%): C, 58.50; H, 4.58; N, 15.78. $C_{26}H_{24}N_6O_7$. Calculated (%): C, 58.66; H, 4.51; N, 15.79. MS, *m/z*: 486 $[M-NO_2]^+$. IR, ν/cm^{-1}: 1350, 1530 (NO_2); 1493 (N(O)N). ^1H NMR (DMSO-d_6), δ: 0.84 (t, 3 H, CH_3); 1.0—1.5 (m, 6 H, $(CH_2)_3$); 3.33 (dd, 1 H, H_b, $^3J_{H,H}$ = 4.0 and 10.0 Hz); 6.01 (s, 1 H, H_a, $^3J_{H,H}$ < 1 Hz); 7.47 (t, 2 H, H_o, Ph); 7.57 (t, 2 H, H_m, Ph); 7.87 (d, 2 H, H_o, Ar^1); 8.02 (d, 1 H, H_p, Ph); 8.24 (2 H, H_o, Ar^2); 8.28 (d, 2 H, H_m, Ar^1); 8.34 (d, 2 H, H_m, Ar^2). ^{13}C NMR, δ: 13.90 (C(6)); 22.41 (C(5)); 29.53 (C(4)); 29.99 (C(3)); 60.35 (CH_b); 97.98 (CH_a); 110.21 (C—Ar^1); 122.05 (C_o, Ph); 123.76 (C_m, Ar^1); 124.18 (C_m, Ar^2); 128.02 (C_o, Ar^1); 128.58 (C_o, Ar^2); 129.09 (C_m, Ph); 131.69, 132.47 (C_p, Ph); 142.26, 146.78, 148.67 (C_p, Ar^1); 149.39, 157.45. ^{14}N NMR, δ: −16 (NO_2, $\Delta\nu_{1/2}$ = 500 Hz); −51 (N(O)=N, $\Delta\nu_{1/2}$ = 400 Hz). For *cis*-**16**, $^3J_{H_a,H_b}$ = 5 Hz (found by comparing the spectrum of *cis,trans*-**16** with the spectrum of *trans*-**16**).

The work was carried out in the Scientific Educational Center of the Institute of Organic Chemistry of the RAS with financial support of the Russian Foundation for Basic Research (Project No. 93-03-18461).

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Received November 1, 1994