Intramolecular interaction between *ortho*-azido and azoxy groups as a new way of forming a N—N bond. Synthesis of 2-alkylbenzotriazole 1-oxides*

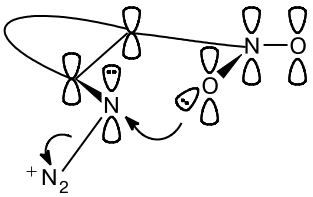
D. L. Lipilin, E. E. Karslyan, A. M. Churakov, Yu. A. Strelenko, and V. A. Tartakovsky*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: churakov@ioc.ac.ru

Heating of 2-(alkyl-*NNO*-azoxy)-1-azidobenzenes in boiling benzene gave 2-alkylbenzotriazole 1-oxides (Alk = Me, Et, Pr^i, and Bu^t). This first-order reaction involves an earlier unknown intramolecular interaction between the azido and azoxy groups with simultaneous release of molecular nitrogen. The cyclization rate increases in the following sequence of the alkyl groups: Me < Et < Pr^i < Bu^t. Complete assignment of the signals in the ^1H, ^{13}C, and ^{14}N NMR spectra of 2-alkylbenzotriazole 1-oxides was performed.

Key words: azides; azoxy compounds; nitrogen-containing heterocycles; *N*-oxides of heterocycles; benzotriazoles; cyclization; ^1H, ^{13}C, and ^{14}N NMR spectroscopy; synthetic methods.

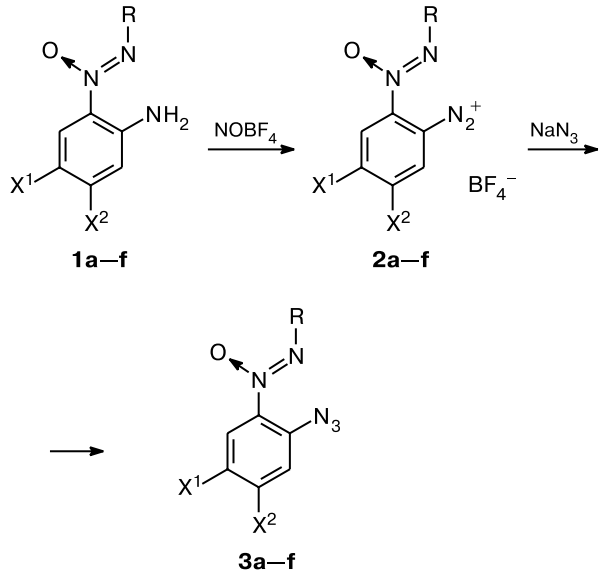
Thermolysis of *o*-nitrophenylazides yields benzofuroxanes, with accompanying evolution of nitrogen. This reaction is well studied.[1] Apparently, its mechanism involves a cyclic transition state in which the lone electron pair of the O atom of the nitro group attacks the electrophilic N atom of the azido group in the plane of the molecule, while the aromatic character of the resulting compound is due to the overlap of the π-orbitals and the lone electron pair of the azido group in the perpendicular plane.[2]



In the present work, we studied an intramolecular interaction between azido and azoxy groups *ortho* to each other. The azoxy group is isoelectronic with the nitro group; as expected, the mechanism of the reaction studied is analogous to the formation of benzofuroxanes, except that the resulting bond is N—N rather than N—O.

Preparation of the starting reagents. Diazonium salts were synthesized by diazotization of 2-(alkyl-*NNO*-azoxy)anilines **1a—f** with nitrosonium tetrafluoroborate according to earlier described procedures.[3] Treatment of diazonium salts **2a—f** with sodium azide gave the starting 1-azido-2-(alkyl-*NNO*-azoxy)benzenes **3a—f** (Scheme 1).

Scheme 1



Compound(s) **1—3**	R	X^1	X^2
a	Me	H	H
b	Et	H	H
c	Pr^i	H	H
d	Bu^t	H	H
e	Bu^t	H	Br
f	Bu^t	Br	H

* Dedicated to Corresponding Member of the Russian Academy of Sciences E. P. Serebryakov on the occasion of his 70th birthday.

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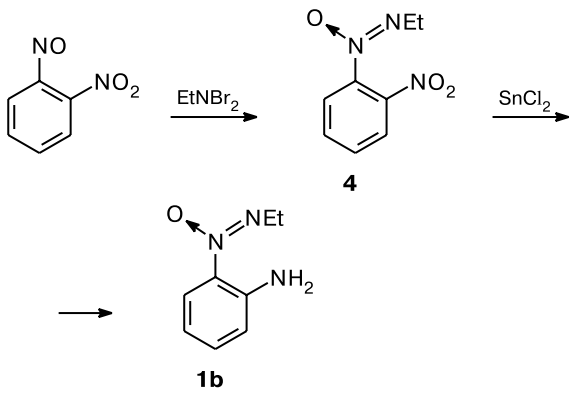
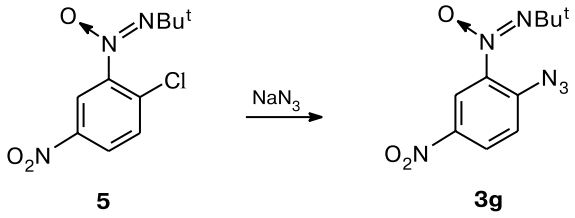
Aniline **1b** was obtained from compound **4** by reduction of the nitro group (Scheme 2). Compound **4** was synthesized by treatment of 1-nitro-2-nitrosobenzene with ethylamine hydrochloride in the presence of dibromoisocyanuric acid. Analogous syntheses of anilines **1a** and **1c**—**f** were described earlier.[4,5]

Scheme 2



Azidobenzene **3g** was obtained by treatment of chloro derivative **5** with sodium azide in DMF at room temperature (Scheme 3).

Scheme 3



All new compounds were identified by ^{1}H, ^{13}C, and ^{14}N NMR spectra with completely assigned signals (see Experimental).

Cyclization of 1-azido-2-azoxybenzenes 3. Heating of azidobenzenes **3a**—**g** in boiling benzene was accompanied by nitrogen evolution, giving rise to the corresponding 2-alkylbenzotriazole 1-oxides **6a**—**g** in virtually quantitative yields (Scheme 4, Table 1).

The cyclization process was monitored by ^{1}H NMR spectroscopy (concentrations of the starting reagents and the reaction products were determined by integration of signals for the corresponding alkyl groups). It was found that the reaction obeys the first-order kinetic equation. The rate constants (Table 2) were calculated by integrated method of substitution (for compound **3a**, the rate constant was determined in two independent experiments over three and seven points; for the other compounds, in one experiment over six points).

Scheme 4

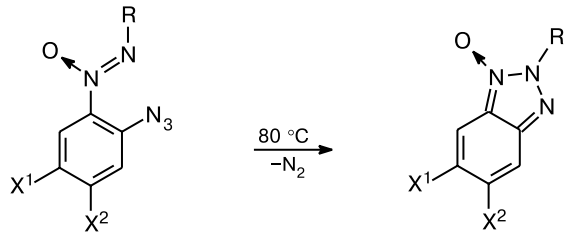


Table 1. Synthesis of benzotriazole 1-oxides **6a**—**g** by cyclization of azidobenzenes[a] **3a**—**g**

Starting reagent	Product	R	X^1	X^2	t^b/h	Yield[c] (%)	M.p. /°C
3a	**6a**	Me	H	H	8	98	95—97[d]
3b	**6b**	Et	H	H	7	95	92—94
3c	**6c**	Pr^i	H	H	6	93	90—93
3d	**6d**	Bu^t	H	H	4	95	96—98[e]
3e	**6e**	Bu^t	H	Br	4	98	92—94
3f	**6f**	Bu^t	Br	H	4	98	86—88
3g	**6g**	Bu^t	NO_2	H	0.5	99	127—129

[a] Benzene, 80 °C.
[b] Reaction duration.
[c] The yield was determined from ^{1}H NMR data.
[d] *Cf.* Ref. 6: m.p. 96 °C.
[e] *Cf.* Ref. 7: m.p. 97—98 °C.

Table 2. Rate constants of the cyclization[a] of azidobenzenes **3** into benzotriazole 1-oxides **6**

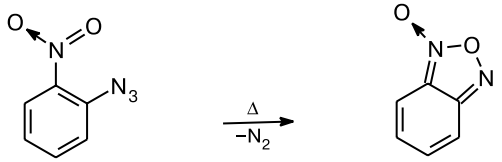
Starting reagent	Product	$k \cdot 10^4/s^{-1}$
3a	**6a**	0.65±0.04
3b	**6b**	0.78±0.08
3c	**6c**	1.00±0.12
3d	**6d**	1.46±0.08
3g	**6g**	15.0±0.3

[a] Benzene, 80 °C.

The data in Table 2 provide clear evidence that the cyclization rate increases in parallel with the electron-donating properties of the alkyl group in the following order: Me < Et < Pr^i < Bu^t. Accordingly, the distal N atom of the azoxy group can be regarded as a nucleophilic reactive center. Since introduction of a nitro group into the *para*-position relative to the azido group accelerates the reaction almost 10 times, the azido group can be considered to be an electrophilic reactive center. Hence, the cyclization mechanism seems to be similar to the thoroughly studied mechanism of the formation of benzofuroxanes **8** in the thermolysis of 2-azido-1-nitroben-

zenes[1] **7**, except that the latter cyclization involves the O atom as a nucleophilic center (Scheme 5).

Scheme 5

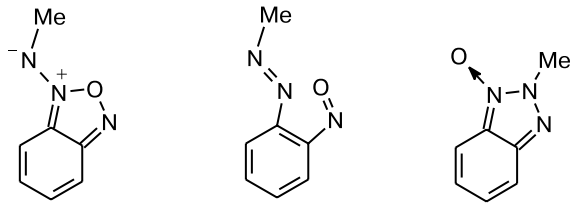


7 **8**

A priori, the oxygen atom could also be a nucleophilic center in the cyclization of 1-azido-2-azoxybenzenes **3** as well. In this case, in the cyclization of, *e.g.*, compound **3f**, *N*-imine **9a** would be a reaction product, which could undergo ring opening to give *ortho*-nitrosoazobenzene **10a** followed by recyclization into thermodynamically more stable *N*-oxide **6e** (Scheme 6). The bromine atom that is *meta* to nitrogen bearing the *N*-oxide oxygen atom in the starting compound **3f** would occupy the *para*-position with respect to such a N atom in reaction product **6e**.

To verify that the sequence **9a** → **10a** → **6e** is thermodynamically favorable, we performed HF/6-31G calculations of the total energies of model compounds **6a**, **9b**, and **10b**.

However, one can unambiguously state that the hypothetical process **3f** → **9a** → **10a** → **6e** does not occur in reality since the thermolysis of azidoazoxybenzene **3f** gives *N*-oxide **6f**, in which the bromine atom is again *meta* to the nitrogen atom bound to the *N*-oxide oxygen atom, as in the starting compound **3f**. Note that benzotriazole 1-oxide **6f** was identified unambiguously. Cyclization of



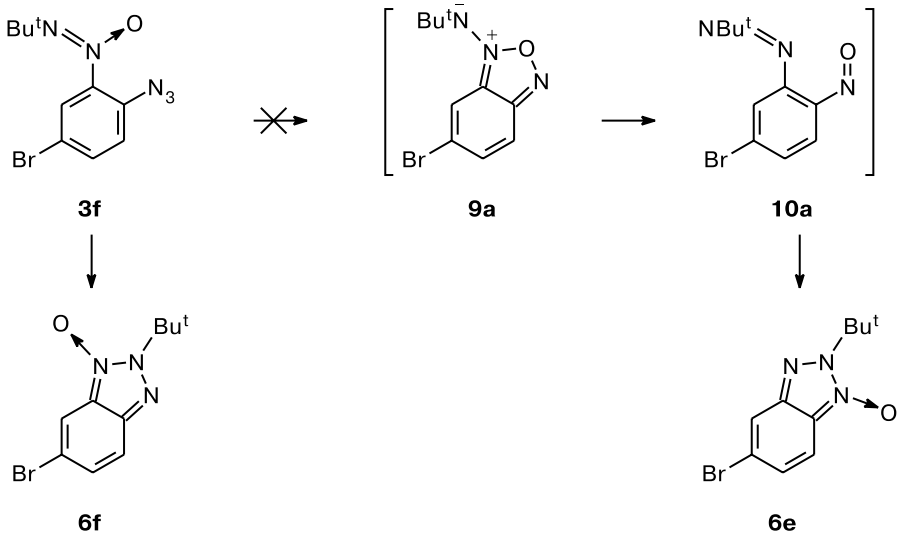
9b 49.1 kcal mol^{-1} **10b** 9.5 kcal mol^{-1} **6a** 0 kcal mol^{-1}

azide **3f** into *N*-oxide **6f** rather than *N*-imine **9a** is probably due to a large energy difference between these compounds (~50 kcal mol^{-1}, which is of the same order as the difference between compounds **6a** and **9b**).

To compare the cyclization rates of compounds **3d** (intramolecular interaction between the azido and azoxy groups) and **7** (intramolecular interaction between the azido and nitro groups), we carried out the following kinetic experiment. A solution of equal amounts of compounds **3d** and **7** in benzene and toluene was heated. Their concentration changes were monitored by recording ^{14}N NMR spectra of periodically withdrawn samples and measuring the integral intensities of the signals for the nitro and azoxy groups. Construction of a linear relationship between the concentrations of the starting reagents and least-squares determination of the ratio of their rate constants[8] showed that the cyclization rate of 2-azido-1-(*tert*-butyl-*NNO*-azoxy)benzene **3d** is 1.4 times higher than that of 2-azido-1-nitrobenzene **7**.

Laboratory preparation of 2-alkylbenzotriazole 1-oxides. 2-Arylbenzotriazole 1-oxides are widely known[9] and their biological activities have been studied in detail.[10] In contrast, 2-alkyl analogs are not easily accessible and have been synthesized only in a few studies.[6,11,12]

Scheme 6

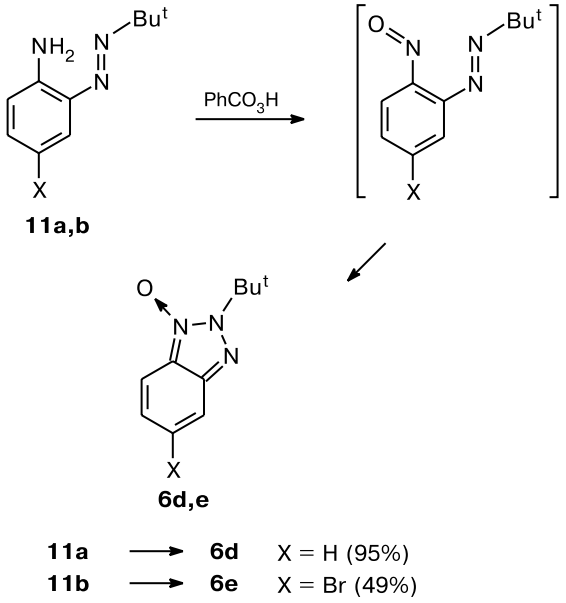


3f **9a** **10a**

6f **6e**

Previously,[7] we reported that oxidation of 2-(*tert*-butylazo)aniline **11a** with perbenzoic acid affords 2-(*tert*-butyl)benzotriazole 1-oxide (**6d**). Using a modified procedure, we increased the yield of this reaction to 95%. However, the oxidation of 4-bromoaniline **11b** gave benzotriazole 1-oxide **6e** only in 49% yield and some by-products were obtained (Scheme 7).

Scheme 7

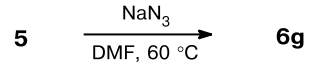


Taking into account that azoanilines **11** are prepared by reduction of the corresponding azoxyanilines **1**,[13] this route to 2-alkylbenzotriazole 1-oxides has no advantages in the synthesis of benzotriazole 1-oxides with electron-withdrawing substituents in the benzene ring.

Laboratory preparation of 2-alkylbenzotriazole 1-oxides **6** from azoxyanilines **1** can be simplified by carrying out the reactions without isolating intermediate products. Such a possibility was illustrated with the transformation **1d** → **6d** in 62% yield.

Alternatively, laboratory preparation of 2-alkylbenzotriazole 1-oxides with electron-withdrawing substituents can be simplified by using 2-chloro-1-azoxybenzenes as starting reagents. For instance, 6-nitrobenzotriazole 1-oxide **6g** was obtained in one step from chloro derivative **5** in 92% yield without isolation of intermediate azidobenzene **3g** (Scheme 8).

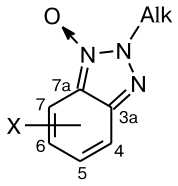
Scheme 8



Spectroscopic studies of 2-alkylbenzotriazole 1-oxides. Complete signal assignment in the ^{1}H (Tables 3, 4), ^{13}C (Table 5), and ^{14}N NMR spectra (Table 6) of 2-alkylbenzotriazole 1-oxides was accomplished. The mass spectra (EI, 70 eV) of these compounds contain a distinct molecular ion peak.

Thus, we studied a new intramolecular cyclization of azido and alkyl-*NNO*-azoxy groups *ortho* to each other. The cyclization rate increases with an increase in both the electron-donating properties of the alkyl group and the electron-withdrawing properties of the substituent *para* to the azido group. This reaction provides a new way of forming a N—N bond. The reaction can be used for labo-

Table 3. ^{1}H NMR spectra (300 MHz, δ, *J*/Hz) of benzotriazole 1-oxides **6a**—**g**



Compound	Alk	X	Solvent	H(4)	H(5)	H(6)	H(7)	Alk
6a	Me	—	CD_2Cl_2	7.68	7.39	7.30	7.68	4.22 s
6b	Et	—	CD_2Cl_2	7.70	7.41	7.32	7.70	1.55 (t, *J* = 7.4); 4.65 (q, *J* = 7.4)
6c	Pr^i	—	CD_2Cl_2	7.70	7.39	7.30	7.70	1.60 (d, *J* = 7.2); 5.48 (hept, *J* = 7.2)
6d	Bu^t	—	CD_2Cl_2	7.68	7.37	7.29	7.66	1.87 s
6e	Bu^t	5-Br	CD_2Cl_2	7.87 (d, *J* = 1.3)	—	7.34 (dd, *J* = 8.8, *J* = 1.3)	7.57 (d, *J* = 8.8)	1.85 s
6f	Bu^t	6-Br	CD_2Cl_2	7.57 (d, *J* = 8.5)	7.41 (dd, *J* = 8.5, *J* = 1.8)	—	7.86 (d, *J* = 1.8)	1.85 s
6g	Bu^t	6-NO_2	Acetone-d_6	7.97 (d, *J* = 8.6)	8.19 (dd, *J* = 8.6, *J* = 1.7)	—	8.58 (d, *J* = 1.7)	1.91 s

Table 4. Spin-spin coupling constants (Hz) in the ABCD-type ^{1}H NMR spectra of benzotriazole 1-oxides **6a—d**

J/Hz	**6a** (Alk = Me)	**6b** (Alk = Et)	**6c** (Alk = Pr^i)	**6d*** (Alk = Bu^t)
$^3J_{H(4),H(5)}$	8.7	8.5	8.6	8.8
$^4J_{H(4),H(6)}$	0.8	1.1	1.1	0.9
$^3J_{H(5),H(6)}$	7.2	6.5	6.7	6.7
$^4J_{H(5),H(7)}$	1.2	0.9	1.1	1.0
$^3J_{H(6),H(7)}$	8.5	8.3	8.6	8.7

* $^5J_{H(4),H(7)}$ = 1.0 Hz.

ratory preparation of not easily accessible 2-alkylbenzotriazole 1-oxides.

Experimental

IR spectra were recorded on a Specord M-80 spectrometer. ^{1}H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AM-300 instrument (300.13, 75.5, and 21.5 MHz, respectively). Chemical shifts in the ^{14}N NMR spectra are given on the δ scale and referenced to $MeNO_2$; upfield shifts are negative. Mass spectra were recorded on a Kratos MS-300 instrument (EI, 70 eV); for bromine-containing fragments, only signals with the ^{79}Br isotope are given. The course of the reactions was monitored by TLC (Silufol UV-254). The earlier described procedures were used to prepare 1-(2-aminophenyl)-2-methyldiazene 1-oxide (**1a**),[5] 1-(2-aminophenyl)-2-isopropyldiazene 1-oxide (**1c**),[5] 1-(2-aminophenyl)-2-(*tert*-butyl)diazene 1-oxide (**1d**),[4] 2-(*tert*-butyl-*NNO*-azoxy)phenyldiazonium tetrafluoroborate (**2d**),[3] 5-bromo-2-(*tert*-butyl-*NNO*-azoxy)phenyldiazonium tetrafluoroborate (**2e**),[3] 4-bromo-2-(*tert*-butyl-*NNO*-azoxy)phenyldiazonium tetrafluoroborate (**2f**),[3] 2-(*tert*-butyl)-1-(2-chloro-5-nitrophenyl)diazene 1-oxide (**5**),[14] 1-(2-aminophenyl)-2-(*tert*-butyl)diazene (**11a**),[13], and 1-(2-amino-5-bromophenyl)-2-(*tert*-butyl)diazene (**11b**).[13]

2-Ethyl-1-(2-nitrophenyl)diazene 1-oxide (4). Ethylamine hydrochloride (245 mg, 3 mmol) was added to a stirred solution of 1-nitro-2-nitrosobenzene (410 mg, 2.7 mmol) in CH_3CN (38 mL); then dibromoisocyanuric acid (900 mg, 3.3 mmol) was added. The reaction mixture was stirred at 24 °C for 5 h (monitoring by TLC); the precipitate of cyanuric acid was filtered off and the filtrate was concentrated *in vacuo*. The product was extracted with CH_2Cl_2 and purified on a thin layer of silica gel with benzene as an eluent. The yield of compound **4** as a red-orange oil was 374 mg (64%). Found (%): C, 49.19; H, 4.61; N, 21.39. $C_8H_9N_3O_3$. Calculated (%): C, 49.23; H, 4.65; N, 21.53. IR (KBr), ν/cm^{-1}: 1492 (N→O); 1360, 1540 (NO_2). ^{1}H NMR (acetone-d_6), δ: 1.34 (t, 3 H, CH_3, J = 7.4 Hz); 3.65 (q, 2 H, CH_2, J = 7.4 Hz); 7.81—7.91 (m, 3 H, Ar); 8.07 (dd, 1 H, Ar, J = 8.8 Hz, J = 1.5 Hz). ^{13}C NMR (acetone-d_6), δ: 11.8 (CH_3); 48.2 (CH_2); 125.8 (CH); 126.3 (CH); 132.4 (CH); 134.8 (CH); 142.5; 144.1. ^{14}N NMR (acetone-d_6), δ: −14 ($\Delta\nu_{1/2}$ = 70 Hz, NO_2); −55 ($\Delta\nu_{1/2}$ = 40 Hz, N(O)=N). MS, m/z: 195 $[M]^+$.

1-(2-Aminophenyl)-2-ethyldiazene 1-oxide (1b). A solution of $SnCl_2 \cdot 2H_2O$ (1.9 g, 8.4 mmol) in conc. HCl (2 mL) was added to a stirred solution of nitro compound **4** (390 mg, 2 mmol) in ethanol (9 mL). The reaction mixture was stirred for 4 h and poured into water. The product was extracted with ethyl acetate and the extract was dried with $MgSO_4$. The solvent was removed and the residue was purified on a thin layer of silica gel with $CHCl_3$ as an eluent. The yield of azoxyaniline **1b** as orange crystals was 240 mg (73%), m.p. 32—34 °C. Found (%): C, 58.39; H, 6.68; N, 25.25. $C_8H_{11}N_3O$. Calculated (%): C, 58.17; H, 6.71; N, 25.44. IR (KBr), ν/cm^{-1}: 1496 (N→O); 3330, 3450 (NH_2). ^{1}H NMR (acetone-d_6), δ: 1.40 (t, 3 H, CH_3, J = 7.1 Hz); 3.69 (q, 2 H, CH_2, J = 7.1 Hz); 6.67 (dt, 1 H, H(4), J = 8.3 Hz, J = 1.3 Hz); 6.96 (dd, 1 H, H(6), J = 8.3 Hz, J = 1.2 Hz); 7.25 (dt, 1 H, H(5), J = 8.4 Hz, J = 1.2 Hz); 7.96 (dd, 1 H, H(3), J = 8.4 Hz, J = 1.3 Hz). ^{13}C NMR (acetone-d_6), δ: 12.8 (CH_3); 47.6 ($\underline{C}Me_3$); 116.6 (C(6)); 119.0 (C(4)); 125.5 (C(3)); 132.8 (C(5)); 143.9 (C(1)). ^{14}N NMR (acetone-d_6), δ: −46 ($\Delta\nu_{1/2}$ = 80 Hz, $\underline{N}$(O)=N); −324 ($\Delta\nu_{1/2}$ = 500 Hz, NH_2). MS, m/z: 165 $[M]^+$.

Synthesis of diazonium tetrafluoroborates 2a—c (general procedure). A solution of azoxyaniline **1** (1.42 mmol) in dry CH_3CN (5 mL) was added dropwise at −15 °C for 10 min to a stirred suspension of $NOBF_4$ (180 mg, 1.56 mmol) in dry CH_3CN (8 mL). The reaction mixture was stirred at −15 °C for 15 min and the solvent was removed by ~90% *in vacuo* at $T \le 0$ °C. The residue was diluted with cooled dry Et_2O. The precipitate of diazonium salt **2** was filtered off, washed with dry Et_2O and pentane, and dried *in vacuo* at $T \le 5$ °C.

2-(Methyl-*NNO*-azoxy)phenyldiazonium tetrafluoroborate (2a). Light yellow crystals, 95% yield, m.p. 98—100 °C

Table 5. ^{13}C NMR spectra (75.5 MHz, CD_2Cl_2, δ, J/Hz) of benzotriazole 1-oxides **6a—g**

Compound	Alk	X	C(3a)	C(4)	C(5)	C(6)	C(7)	C(7a)	Alk
6a	Me	—	141.0	119.1	128.7	126.0	113.8	131.4	36.1
6b	Et	—	141.0	119.3	128.6	126.1	113.8	131.3	13.1, 44.7
6c	Pr^i	—	140.8	119.4	128.4	126.0	113.8	131.2	20.9, 51.7
6d	Bu^t	—	139.5	118.5	128.1	126.1	113.4	127.6	27.2, 66.7
6e	Bu^t	5-Br	140.3	121.8	122.0	129.5	115.3	126.8	27.0, 67.3
6f	Bu^t	6-Br	138.4	121.0	132.2	119.6	116.4	128.8	27.1, 67.3
6g	Bu^t	6-NO_2	141.0	121.5	123.0	145.8	112.7	127.1	26.7, 68.5
			^2J = 5.9, ^3J = 8.6	^1J = 175, ^2J = 3.9	^1J = 171, ^2J = 4.6, ^3J = 9.5	^2J = 4.1, ^2J = 5.9, ^3J = 10.8	^1J = 178, ^3J = 8.4, ^4J = 1.5	^2J = 5.8	

Table 6. ^{14}N NMR spectra (21.7 MHz, CD_2Cl_2, δ) of benzotriazole 1-oxides **6a**—**g**. Parenthetical values refer to $\Delta\nu_{1/2}$/Hz

Compound	N(1)→O	N(2)—R	NO_2
6a	−70 (250)	−135 (600)	—
6b	−91 (150)	−120 (650)	—
6c	−91 (350)	−114 (850)	—
6d	−90 (300)	−116 (700)	—
6e	−89 (400)	−115 (800)	—
6f	−88 (350)	−139 (800)	—
6g	−82 (350)	−95 (850)	−14 (130)

(decomp.). Found (%): C, 33.59; H, 2.79; N, 22.27. $C_7H_7BF_4N_4O$. Calculated (%): C, 33.64; H, 2.82; N, 22.41. IR (KBr), ν/cm^{-1}: 1500 (N→O); 2280 (N_2^+). ^1H NMR (acetone-d_6), δ: 3.61 (s, 3 H, CH_3); 8.32 (ddd, 1 H, H(5), J = 8.0 Hz, J = 7.8 Hz, J = 1.5 Hz); 8.55.(ddd, 1 H, H(4), J = 8.1 Hz, J = 8.0 Hz, J = 1.3 Hz); 8.73 (dd, 1 H, H(3), J = 8.1 Hz, J = 1.5 Hz); 9.04 (dd, 1 H, H(6), J = 7.8 Hz, J = 1.3 Hz). ^{13}C NMR (acetone-d_6), δ: 40.9 (CH_3); 110.8 (C(1)); 127.0 (C(3)); 135.1 (C(5)); 137.8 (C(6)); 143.3 (C(3)); 145.7 (C(2)). ^{14}N NMR (acetone-d_6), δ: −61 ($\Delta\nu_{1/2}$ = 60 Hz, N(O)=N); −154 ($\Delta\nu_{1/2}$ = 160 Hz, N_2^+).

2-(Ethyl-*NNO*-azoxy)phenyldiazonium tetrafluoroborate (2b). Light yellow crystals, 66% yield, m.p. 132—134 °C (decomp.). Found (%): C, 36.21; H, 3.45; N, 21.49. $C_8H_9BF_4N_4O$. Calculated (%): C, 36.40; H, 3.44; N, 21.22. IR (KBr), ν/cm^{-1}: 1500 (N→O); 2300 (N_2^+). ^1H NMR (acetone-d_6), δ: 1.47 (t, 3 H, CH_3, J = 7.4 Hz); 4.86 (q, 2 H, CH_2, J = 7.4 Hz); 8.33 (ddd, 1 H, H(5), J = 8.8 Hz, J = 8.1 Hz, J = 1.5 Hz); 8.58 (ddd, 1 H, H(4), J = 8.4 Hz, J = 8.1 Hz, J = 1.5 Hz); 8.78 (dd, 1 H, H(3), J = 8.4 Hz, J = 1.5 Hz); 9.11 (dd, 1 H, H(6), J = 8.8 Hz, J = 1.5 Hz). ^{13}C NMR (acetone-d_6), δ: 11.8 (CH_3); 49.1 (CH_2CH_3); 110.8 (C(1)); 127.1 (C(3)); 135.1 (C(5)); 137.3 (C(6)); 143.2 (C(4)); 145.8 (C(2)). ^{14}N NMR (acetone-d_6), δ: −64 ($\Delta\nu_{1/2}$ = 80 Hz, N(O)=N); −154 ($\Delta\nu_{1/2}$ = 160 Hz, N_2^+).

2-(Isopropyl-*NNO*-azoxy)phenyldiazonium tetrafluoroborate (2c). Colorless crystals, 79% yield, m.p. 112—114 °C (decomp.). Found (%): C, 38.96; H, 3.98; N, 20.33. $C_9H_{11}BF_4N_4O$. Calculated (%): C, 38.88; H, 3.99; N, 20.15. IR (KBr), ν/cm^{-1}: 1500 (N→O); 2300 (N_2^+). ^1H NMR (acetone-d_6), δ: 1.37 (d, 6 H, 2 CH_3, J = 6.6 Hz); 4.46 (hept, 1 H, CHMe$_2$, J = 6.6 Hz); 8.29 (ddd, 1 H, H(5), J = 8.4 Hz, J = 8.1 Hz, J = 1.5 Hz); 8.55 (ddd, 1 H, H(4), J = 8.4 Hz, J = 8.1 Hz, J = 1.4 Hz); 8.75 (dd, 1 H, H(3), J = 8.4 Hz, J = 1.5 Hz); 9.05 (dd, 1 H, H(6), J = 8.1 Hz, J = 1.4 Hz). ^{13}C NMR (acetone-d_6), δ: 19.3 (CH_3); 54.2 (CHMe$_2$); 110.9 (C(1)); 127.1 (C(3)); 135.0 (C(5)); 137.2 (C(6)); 143.2 (C(4)); 145.9 (C(2)). ^{14}N NMR (acetone-d_6), δ: −66 ($\Delta\nu_{1/2}$ = 80 Hz, N(O)=N); −154 ($\Delta\nu_{1/2}$ = 200 Hz, N_2^+).

Synthesis of 2-(alkyl-*NNO*-azoxy)-1-azidobenzenes 3a—f (general procedure). Sodium azide (130 mg, 2.0 mmol) was added at −10 °C to a stirred solution of diazonium tetrafluoroborate **2** (0.5 mmol) in dry acetone (15 mL). The reaction mixture was stirred at −10 °C for 30 to 60 min (monitoring by TLC) and poured into water. The product was extracted with CH_2Cl_2. The extract was dried with $MgSO_4$ and concentrated *in vacuo* at $T \le 20$ °C. The residue was purified on a thin layer of silica gel with $CHCl_3$ as an eluent.

1-(2-Azidophenyl)-2-methyldiazene 1-oxide (3a). Dark yellow oil, 60% yield. Found (%): C, 47.65; H, 3.93; N, 39.69. $C_7H_7N_5O$. Calculated (%): C, 47.46; H, 3.98; N, 39.53. IR (KBr), ν/cm^{-1}: 1490 (N→O); 2150 (N_3). ^1H NMR (CD_2Cl_2), δ: 3.41 (s, 3 H, CH_3); 7.21—7.27 (m, 2 H, Ar), 7.45—7.51 (m, 2 H, Ar). ^{13}C NMR (CD_2Cl_2), δ: 40.5 (CH_3); 120.7 (C(3)); 125.4 (C(6)); 125.6 (C(5)); 131.6 (C(4)); 133.6 (C(2)); 140.8 (C(1)). ^{14}N NMR (CD_2Cl_2), δ: −48 ($\Delta\nu_{1/2}$ = 90 Hz, N(O)=N); −141 ($\Delta\nu_{1/2}$ = 80 Hz, —N=N=N).

1-(2-Azidophenyl)-2-ethyldiazene 1-oxide (3b). Dark yellow oil, 78% yield. Found (%): C, 50.41; H, 4.70; N, 36.45. $C_8H_9N_5O$. Calculated (%): C, 50.26; H, 4.74; N, 36.63. IR (KBr), ν/cm^{-1}: 1500 (N→O); 2170 (N_3). ^1H NMR (CD_2Cl_2), δ: 1.38 (t, 3 H, CH_3, J = 7.3 Hz); 3.65 (q, 2 H, CH_2, J = 7.3 Hz); 7.18—7.28, 7.45—7.52 (both m, 2 H each, Ar). ^{13}C NMR (CD_2Cl_2), δ: 12.2 (CH_3); 47.9 (CH_2); 120.6 (C(3)); 125.3 (C(6)); 125.5 (C(5)); 131.3 (C(4)); 133.5 (C(2)); 140.9 (C(1)). ^{14}N NMR (CD_2Cl_2), δ: −51 ($\Delta\nu_{1/2}$ = 60 Hz, N(O)=N); −142 ($\Delta\nu_{1/2}$ = 50 Hz, —N=N=N).

1-(2-Azidophenyl)-2-isopropyldiazene 1-oxide (3c). Brown oil, 90% yield. Found (%): C, 52.83; H, 5.37; N, 33.95. $C_9H_{11}N_5O$. Calculated (%): C, 52.67; H, 5.40; N, 34.13. IR (KBr), ν/cm^{-1}: 1490 (N→O); 2130 (N_3). ^1H NMR (CD_2Cl_2), δ: 1.27 (d, 6 H, 2 CH_3, J = 6.7 Hz); 4.60 (h, 1 H, CHMe$_2$, J = 6.7 Hz); 7.18—7.27, 7.44—7.49 (both m, 2 H each, Ar). ^{13}C NMR (CD_2Cl_2), δ: 19.5 (CH_3); 52.4.0 (CHMe$_2$); 120.6 (C(3)); 125.1 (C(6)); 125.5 (C(5)); 131.2 (C(4)); 133.4 (C(2)); 141.5 (C(1)). ^{14}N NMR (CD_2Cl_2), δ: −53 ($\Delta\nu_{1/2}$ = 50 Hz, N(O)=N); −141 ($\Delta\nu_{1/2}$ = 50 Hz, —N=N=N).

1-(2-Azidophenyl)-2-(*tert*-butyl)diazene 1-oxide (3d). Dark yellow oil, 85% yield. Found (%): C, 54.65; H, 5.94; N, 31.73. $C_{10}H_{13}N_5O$. Calculated (%): C, 54.78; H, 5.98; N, 31.94. IR (KBr), ν/cm^{-1}: 1480 (N→O), 2130 (N_3). ^1H NMR (CD_2Cl_2), δ: 1.44 (s, 9 H, Bu^t); 7.25—7.35, 7.41—7.50 (both m, 2 H each, Ar). ^{13}C NMR (CD_2Cl_2), δ: 25.8 (CH_3); 60.2 (CMe$_3$); 120.5 (C(3)), 124.9 (C(6)), 125.4 (C(5)), 130.8 (C(4)), 133.2 (C(2)), 142.1 (C(1)). ^{14}N NMR (CD_2Cl_2), δ: −53.0 ($\Delta\nu_{1/2}$ = 80 Hz, N(O)=N); −142 ($\Delta\nu_{1/2}$ = 90 Hz, —N=N=N). MS, *m/z*: 191 $[M - N_2]^+$.

1-(2-Azido-4-bromophenyl)-2-(*tert*-butyl)diazene 1-oxide (3e). Yellow crystals, 46% yield, m.p. 36—38 °C (decomp. at 68 °C). Found (%): C, 40.45; H, 4.11; Br, 26.98; N, 23.25. $C_{10}H_{12}BrN_5O$. Calculated (%): C, 40.29; H, 4.06; Br, 26.80; N, 23.49. IR (KBr), ν/cm^{-1}: 1480 (N→O); 2120 (N_3). ^1H NMR (CD_2Cl_2), δ: 1.43 (s, 9 H, Bu^t); 7.48 (dd, 1 H, H(5), J = 9.3 Hz, J = 1.3 Hz); 7.76 (d, 1 H, H(6), J = 9.3 Hz); 8.08 (d, 1 H, H(3), J = 1.3 Hz). ^{13}C NMR (CD_2Cl_2), δ: 25.70 (CH_3), 60.4 (CMe$_3$), 123.6 (C(3)), 124.0 (C(4)), 126.2 (C(6)), 128.5 (C(5)), 134.8 (C(2)), 141.0 (C(1)). ^{14}N NMR (CD_2Cl_2), δ: −54 ($\Delta\nu_{1/2}$ = 70 Hz, N(O)=N); −142 ($\Delta\nu_{1/2}$ = 150 Hz, —N=N=N).

1-(2-Azido-5-bromophenyl)-2-(*tert*-butyl)diazene 1-oxide (3f). Yellow crystals, 70% yield, m.p. 72—76 °C (decomp.). Found (%): C, 40.33; H, 4.09; Br, 26.69; N, 23.20. $C_{10}H_{12}BrN_5O$. Calculated (%): C, 40.29; H, 4.06; Br, 26.80; N, 23.49. IR (KBr), ν/cm^{-1}: 1490 (N→O); 2140 (N_3). ^1H NMR (CD_2Cl_2), δ: 1.44 (s, 9 H, Bu^t); 7.11 (d, 1 H, H(3), J = 8.6 Hz); 7.55 (dd, 1 H, H(4), J = 8.6 Hz, J = 2.1 Hz); 7.59 (d, 1 H, H(6), J = 2.1 Hz). ^{13}C NMR (CD_2Cl_2), δ: 25.7 (CH_3), 60.5 (CMe$_3$), 117.4 (C(5)), 122.1 (C(3)), 128.1 (C(6)), 132.6 (C(2)), 133.8 (C(4)), 142.3 (C(1)). ^{14}N NMR (CD_2Cl_2), δ: −55 ($\Delta\nu_{1/2}$ = 90 Hz, N(O)=N); −142 ($\Delta\nu_{1/2}$ = 80 Hz, —N=N=N).

1-(2-Azido-5-nitrophenyl)-2-(*tert*-butyl)diazene 1-oxide (3g). Sodium azide (130 mg, 2.0 mmol) was added at −10 °C to a

stirred solution of chloro derivative **5** (50 mg, 0.194 mmol) in DMF (5 mL). The reaction mixture was stirred at 20 °C for 4 h and poured into water. The product was extracted with CH_2Cl_2 and the extract was dried with $MgSO_4$ and concentrated *in vacuo* at $T \le 20$ °C. The products were separated off by column chromatography on silica gel with EtOAc—light petroleum (1 : 7) as an eluent to give azide **3g** (29 mg, 56%) and benzotriazole 1-oxide **6g** (18 mg, 38%). Azide **3g**: yellow crystals, m.p. 96—98 °C (decomp.). Found (%): C, 45.61; H, 4.54; N, 31.57. $C_{10}H_{12}N_6O_3$. Calculated (%): C, 45.45; H, 4.58; N, 31.80. IR (KBr), ν/cm^{-1}: 1510 (N→O); 1380, 1520 (NO_2); 2160 (N_3). ^{1}H NMR (CD_2Cl_2), δ: 1.43 (s, 9 H, Bu^t); 7.38 (d, 1 H, J = 8.5 Hz); 8.27—8.31 (m, 2 H, H(4) and H(6)). ^{13}C NMR (CD_2Cl_2), δ: 25.6 (CH_3), 60.8 ($\underline{C}Me_3$), 121.1 (C(6)), 121.2 (C(3)), 125.9 (C(4)), 140.2 (C(2)), 140.9 (C(1)), 144.1 (C(5)). ^{14}N NMR (CD_2Cl_2), δ: −16 ($\Delta\nu_{1/2}$ = 210 Hz, NO_2), −57 ($\Delta\nu_{1/2}$ = 110 Hz, $\underline{N}$(O)=N), 144 ($\Delta\nu_{1/2}$ = 130 Hz, —N=$\underline{N}$=N).

Synthesis of 2-alkylbenzotriazole 1-oxides 6a—g (general procedure). A solution of 2-(alkyl-*NNO*-azoxy)-1-azidobenzene **3** (1.0 mmol) in benzene (10 mL) was refluxed for a period of time specified in Table 1. After the reaction was completed (monitoring by TLC), the solvent was removed *in vacuo*. When necessary, the product was purified on a thin layer of silica gel with $CHCl_3$ as an eluent.

2-Methyl-2*H*-1,2,3-benzotriazole 1-oxide (6a). Light yellow crystals, 85% yield. Found (%): C, 56.52; H, 4.74; N, 28.32. $C_7H_7N_3O$. Calculated (%): C, 56.37; H, 4.73; N, 28.17. MS, *m/z*: 149 $[M]^+$.

2-Ethyl-2*H*-1,2,3-benzotriazole 1-oxide (6b). Light yellow crystals, 93% yield. Found (%): C, 59.03; H, 5.54; N, 25.59. $C_8H_9N_3O$. Calculated (%): C, 58.88; H, 5.56; N, 25.75. MS, *m/z*: 163 $[M]^+$.

2-Isopropyl-2*H*-1,2,3-benzotriazole 1-oxide (6c). Light yellow crystals, 90% yield. Found (%): C, 60.88; H, 6.24; N, 23.89. $C_9H_{11}N_3O$. Calculated (%): C, 61.00; H, 6.26; N, 23.71. MS, *m/z*: 177 $[M]^+$.

2-(*tert*-Butyl)-2*H*-1,2,3-benzotriazole 1-oxide (6d). Light yellow crystals, 95% yield. MS, *m/z*: 191 $[M]^+$.

5-Bromo-2-(*tert*-butyl)-2*H*-1,2,3-benzotriazole 1-oxide (6e). Colorless crystals, 95% yield. Found (%): C, 44.59; H, 4.47; Br, 29.71; N, 15.38. $C_{10}H_{12}BrN_3O$. Calculated (%): C, 44.46; H, 4.48; Br, 29.58; N, 15.56. MS, *m/z*: 269 $[M]^+$.

6-Bromo-2-(*tert*-butyl)-2*H*-1,2,3-benzotriazole 1-oxide (6f). Light yellow crystals, 95% yield. Found (%): C, 44.33; H, 4.45; Br, 29.79; N, 15.47. $C_{10}H_{12}BrN_3O$. Calculated (%): C, 44.46; H, 4.48; Br, 29.58; N, 15.56. MS, *m/z*: 269 $[M]^+$.

2-(*tert*-Butyl)-6-nitro-2*H*-1,2,3-benzotriazole 1-oxide (6g). Bright yellow crystals, 90% yield. Found (%): C, 51.06; H, 5.11; N, 23.95. $C_{10}H_{12}N_4O_3$. Calculated (%): C, 50.84; H, 5.12; N, 23.72. MS, *m/z*: 236 $[M]^+$.

Synthesis of benzotriazole 1-oxide 6d by oxidation of 2-(*tert*-butylazo)aniline (11a) with perbenzoic acid. A solution of azoaniline **11a** (100 mg, 0.565 mmol) in CH_2Cl_2 (3 mL) was added dropwise at 0 °C to a solution of perbenzoic acid (250 mg, 1.81 mmol) in Et_2O (12 mL). The reaction mixture was kept at 4 °C for 16 h. The excess of perbenzoic acid was removed by treatment with 20% aqueous KI (5 mL). Then 20% aqueous $Na_2S_2O_3$ (5 mL) was added. The organic phase was separated, washed with concentrated aqueous $NaHCO_3$ (5×10 mL) and brine (2×10 mL), and dried with $CaCl_2$. The solvent was removed *in vacuo* and the residue was purified on a thin layer of silica gel with $CHCl_3$ as an eluent to give compound **6d** (103 mg, 95%) as light yellow crystals identical with an authentic sample.

Synthesis of 5-bromobenzotriazole 1-oxide 6e by oxidation of 4-bromo-2-(*tert*-butylazo)aniline (11b) with perbenzoic acid. The reaction of azoaniline **11b** with $PhCO_3H$ according to the above procedure followed by column chromatography of the residue on silica gel with $CHCl_3$—EtOAc (4 : 1) as an eluent gave 5-bromobenzotriazole 1-oxide **6e** in 49% yield. The product was identical with an authentic sample.

Synthesis of benzotriazole 1-oxide 6d without isolation of intermediates. A solution of 1-(2-aminophenyl)-2-(*tert*-butyl)diazene 1-oxide **1d** (750 mg, 3.68 mmol) in dry MeCN (13 mL) was added dropwise at −15 °C for 10 min to a stirred suspension of $NOBF_4$ (480 mg, 4.0 mmol) in dry MeCN (19 mL). The solution was stirred at −15 °C for an additional 15 min and diluted with dry acetone (80 mL). Sodium azide (960 mg, 14.7 mmol) was added and the reaction mixture was stirred at −10 °C for 1 h and poured into water. The product was extracted with benzene (3×15 mL), dried with $MgSO_4$, and refluxed for 4 h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel with $CHCl_3$ as an eluent to give benzotriazole 1-oxide **6d** (440 mg, 62%). The product was identical with an authentic sample.

Synthesis of 6-nitrobenzotriazole 1-oxide 6g without isolation of intermediates. Sodium azide (81 mg, 1.24 mmol) was added to a stirred solution of chloro derivative **5** (32 mg, 0.124 mmol) in DMF (6 mL). The reaction mixture was stirred at 60—65 °C for 1 h and poured into water. The product was extracted with CH_2Cl_2 and dried with $MgSO_4$. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel with $CHCl_3$ as an eluent to give benzotriazole 1-oxide **6g** (27 mg, 92%). The product was identical with an authentic sample.

Kinetic experiments

Comparison of the decomposition rates of 2-azido-1-nitrobenzene (7) and 2-azido-1-(*tert*-butyl-*NNO*-azoxy)benzene (3d). A mixture of compound **3d** (100.4 mg, 0.467 mmol) and 2-azido-1-nitrobenzene **7** (74.72 mg, 0.467 mmol) was dissolved in a mixture of C_6H_6 (2 mL) and $C_6H_5CD_3$ (0.6 mL). The resulting solution was transferred to a tube and the tube was placed in a thermostat (T = 80 °C). Five samples were withdrawn from the reaction mixture at 20-min intervals and their ^{14}N NMR spectra were recorded. Using the integral intensities of the signals for the nitro group of 2-azido-1-nitrobenzene (**7**) (δ −13) and for the azoxy group of compound **3d** (δ −48), we plotted a linear relationship between the concentration changes of the starting reagents according to the general equation:[8]

$$\frac{1/\nu_i(c_i - c_{j,0})}{1/\nu_k(c_k - c_{k,0})} = \frac{k_j}{k_k},$$

where $\nu_j(c_j - c_{j,0})$ is the concentration of product j, $\nu_k(c_k - c_{k,0})$ is the concentration of product k, k_j is the reaction rate constant for compound j, and k_k is the reaction rate constant for compound k.

Least-squares determination of the ratio of the cyclization rate constants of compounds **3d** and **7** gave 1 : 1.4±0.08.

Determination of the reaction order and the decomposition rate constant of 2-azido-1-(methyl-*NNO*-azoxy)benzene (3a). A solution of compound **3a** (46 mg, 0.26 mmol) in C_6H_6 (3 mL)

was placed in a thermostat (T = 80 °C). Seven samples were withdrawn at 30-min intervals. The solvent was removed *in vacuo* at a bath temperature no higher than 20 °C. The sample concentrations of compound **3a** were determined from the integral intensities of the signal for the methyl group (δ 3.41) in the ^{1}H NMR spectra with consideration of the integral intensity of the signal for the methyl group in the final product **6a** (δ 4.22). An analogous experiment was carried out for the same initial concentration of compound **3a** (C = 0.875 mmol mL^{-1}), while withdrawing three samples at 1-h intervals. Using the integral substitution method,[15] we found this reaction to obey the first-order kinetics. The rate constant of this reaction with a standard deviation ($10^4 \cdot k$ = 0.65±0.04 s^{-1}) was obtained by statistical processing of the constants (determined from the equation $kt = \ln(C_0/C)$ for different C_0 and C values) with consideration of the t-test value.[16]

Determination of the decomposition rate constants of azides 3b—d,g. A solution of an azide in C_6H_6 (C = 0.1 mmol mL^{-1}) was placed in a thermostat (T = 80 °C). Six samples were withdrawn at equal intervals (45 min for **3b**, 30 min for **3c,d**, and 5 min for **3g**). The current azide concentrations were determined from the integral intensities of signals for the alkyl groups in the ^{1}H NMR spectra as described above, which were used to calculate the decomposition rate constants.

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