2-Alkyl-4-amino-5-(*tert*-butyl-*NNO*-azoxy)-2*H*-1,2,3-triazole 1-oxides: synthesis and reduction*

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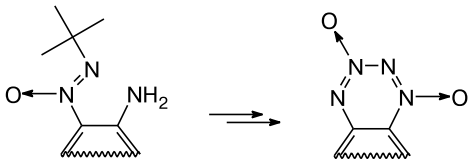
A new approach to the synthesis of 4-amino-5-(*tert*-butyl-*NNO*-azoxy)-2-R-2*H*-1,2,3-triazole 1-oxides **1** was developed. Compounds **1** were obtained by reactions of 3-amino-4-(*tert*-butyl-*NNO*-azoxy)furoxan with aliphatic amines RNH_2 (R = Me, Et, Pr^i, Bu, and Bu^t). 4-Amino-5-(*tert*-butyl-*NNO*-azoxy)-2-*tert*-butyl-2*H*-1,2,3-triazole 1-oxide was transformed under the action of acids into 4-amino-5-(*tert*-butyl-*NNO*-azoxy)-1-hydroxy-1*H*-1,2,3-triazole. Methylation of the latter with diazomethane mainly involves the O atom of the triazole oxide ring. Reduction of compounds **1** gave 4-amino-5-(*tert*-butyl-*NNO*-azoxy)-2-R-2*H*-1,2,3-triazoles and 4-amino-5-(*tert*-butyldiazenyl)-2-R-2*H*-1,2,3-triazoles (R = Me, Pr^i, and Bu^t). The structures of the compounds obtained were confirmed by ^1H, ^{13}C, and ^{14}N NMR spectroscopy.

Key words: 1,2,3-triazole 1-oxides, 1,2,3-triazoles, *tert*-butylazoxy group, aminofuroxans, alkylation, methylation, ^1H, ^{13}C, and ^{14}N NMR spectroscopy.

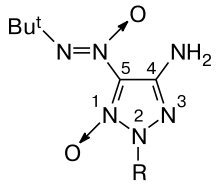
Earlier,[1] our research team has developed a method for the synthesis of annulated 1,2,3,4-tetrazine 1,3-dioxides (TDO) from arenes containing vicinal *tert*-butylazoxy and amino groups (Scheme 1).

Scheme 1



Benzotetrazine 1,3-dioxides are studied most comprehensively. At the same time, TDO annulated to heterocyclic rings are of great interest for the chemistry of nitrogen-containing systems because they can be used as high-energy and biologically active compounds. 1,2,3,4-Tetrazine 1,3-dioxides annulated to the furazan[2] and pyridine rings[3] have been obtained to date. The present work deals with the synthesis of triazole oxides **1** and triazoles **2**. The latter are the starting materials for the synthesis of TDO annulated with the triazole ring.

Synthesis of triazole oxides 1. 2-Alkyl-4-amino-5-nitro-2*H*-1,2,3-triazole 1-oxides are close structural analogs of



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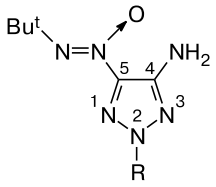

2

compounds **1**. One of the known routes to these compounds involves reactions of 4-amino-3-nitrofuroxan with primary amines in CH_2Cl_2.[4—6]

Keeping this in mind, here we studied reactions of primary amines with the recently synthesized[7] amino-(*tert*-butyl-*NNO*-azoxy)furoxan **3** showing the fast isomerism **3a** ↔ **3b** in solutions (Scheme 2).

The best results were achieved in a reaction of furoxan **3** with Bu^tNH_2. Under the optimized conditions, the yield of triazole oxide **1d** amounts to 80% (Table 1). The yields of triazole oxides **1** obtained from $MeNH_2$, $EtNH_2$, and Pr^iNH_2 are 30—34%; the use of $BuNH_2$ lowers the yield to 12%. Low-boiling amines ($MeNH_2$ and $EtNH_2$) can conveniently be employed as hydrochlorides *in situ* releasing the free amine upon the addition of Na_2CO_3 (method ***A***). With the synthesis of triazole oxide **1a** as an example, we demonstrated that its yield is independent of whether the free amine or its hydrochloride is used. The reaction rate increases in the presence of the excess amines; however, this lowers the yield of the target product (for Pr^iNH_2 and $BuNH_2$). With Bu^tNH_2, the yield is virtually unaffected by the excess amine.

*Dedicated to Academician of the Russian Academy of Sciences A. I. Konovalov on the occasion of his 80th birthday.

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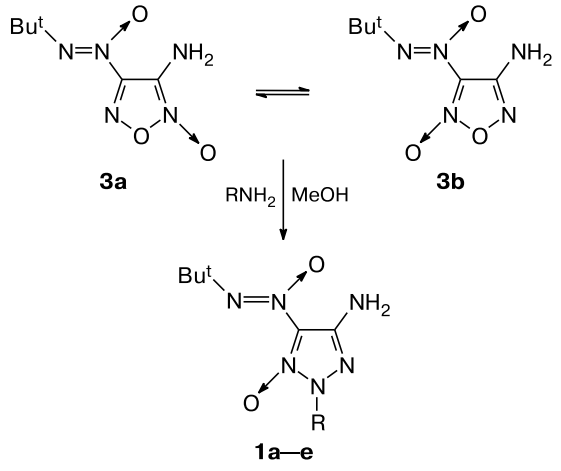
Scheme 2



R = Me (**a**), Et (**b**), Pr^i (**c**), Bu^t (**d**), Bu (**e**)

Methanol was used as a solvent because the reactions in $CHCl_3$ provide lower yields of the products[8] (see Table 1). The reaction can be carried out both at room temperature (method ***B***) and in boiling methanol (method ***C***).

The plausible mechanism of the reaction. Crystalline furoxan **3** consists almost entirely of individual isomer **3a**.[7] However, its dissolution promptly gives rise to the second isomer **3b**. Heating increases the isomerization rate: in boiling methanol, the process reaches equilibrium in a few minutes, and the content of isomer **3b** is ~20%. Therefore, furoxan **3** isomerizes more readily than do most nonannulated furoxans.[9] Apparently, this is due to the stabilization of the dinitrosoethene intermediate **3c** (see Ref. 10) by conjugation of the vicinal amino and nitroso groups (Scheme 3, resonance structure **3c´**).

In reactions of primary amines with furoxan **3**, the amine could formally react with both cyclic isomers (**3a** or **3b**) and the open form **3c**, which is present in solution in some amount. The latter pathway seems to be most likely (see Scheme 3). One can see in Scheme 3 that the character of the conjugation in the open form **3c** makes the nitroso groups different in electrophilicity. The nitroso group at the carbon atom bearing the amino group is more electrophilic than the neighboring nitroso group and hence will interact with the amine to give azo compound **4** undergoing cyclization into triazole 1-oxide **1**. This mechanism explains why the reaction yields only one isomer of the triazole 1-oxide.

Scheme 3

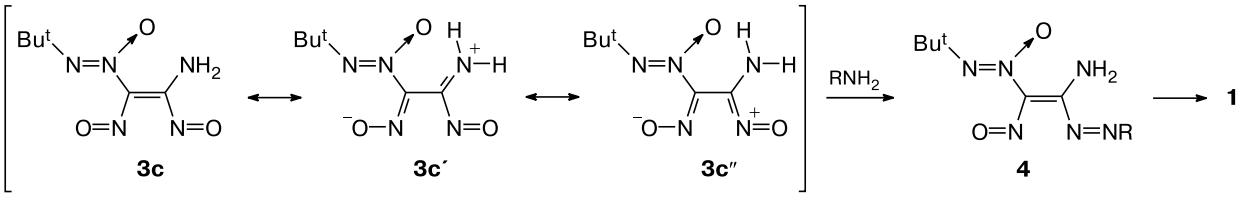
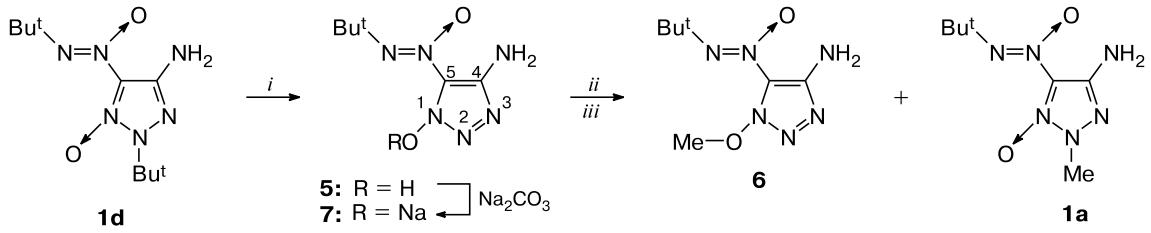


Table 1. Synthesis of 1,2,3-triazole 1-oxides **1a—e**

Compound	Amine	Method	N^a	Solvent	T/°C	τ/h	Yield (%)
1a	$MeNH_2$	***A***^{b}, ***B***	1	MeOH	25	24	30
1b	$EtNH_2$	***A***^{b}	1	MeOH	25	24	34
1c	Pr^{i}NH$_2$	***B***	3	MeOH	25	0.3	20
			1	MeOH	25	2	34
			1	$CHCl_3$	25	6.5	17
		C	1	MeOH	64	0.4	34
1d	Bu^{t}NH$_2$	***B***	5	MeOH	25	1.5	69
			1	MeOH	25	10	73
			1.4	$CHCl_3$	25	24	44
		C	1	MeOH	64	1.5	80
1e	$BuNH_2$	***B***	4	MeOH	25	0.3	0
			1	MeOH	25	8	12
			2	$CHCl_3$	10—15	2.5	6

[a] The mole number of the amine per mole of compound **3a**.
[b] The free amine was generated *in situ* from its hydrochloride by addition of Na_2CO_3.

Scheme 4



i. CF_3CO_2H, 25 °C, 15 min (98% yield of **5**); conc. HCl, AcOEt, 25 °C, 30 min (100% yield of **5**); *ii.* **5**, CH_2N_2 in Et_2O, MeCN, 5—10 °C, 5 min (80% yield of **6**) or *iii.* **7**, Me_2SO_4, acetone, 25 °C, 4 h (45% yield of **6**; 5% yield of **1a**).

Methylation of hydroxytriazole 5. When treated with HCl or CF_3CO_2H, triazole oxide **1d** easily eliminates the *tert*-butyl group to form 1-hydroxytriazole **5** (Scheme 4) (see Ref. 8). A reaction of this compound with diazomethane affords O-methylated derivative **6**. A sodium salt of triazole oxide (**7**) reacts with dimethyl sulfate, also giving compound **6** as a major product. In this case, N-alkylation at the N(2) atom is only slight.

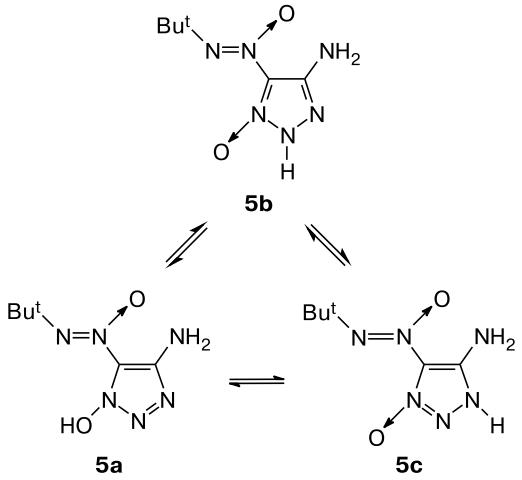
The ^{1}H NMR spectrum of hydroxytriazole **5** in dry DMSO-d_6 contains a signal for the *tert*-butyl group, a broadened signal at δ 5.9 with the integral intensity corresponding to two protons (NH_2), and a strongly broadened signal at δ 13.7 with an integral intensity of 1 H. This proton can be bound to the O atom (**5a**) or to the N atoms of the triazole ring (**5b** and **5c**) (Scheme 5).

The IR spectrum of crystalline compound **5** (in KBr pellets) shows a wide endocyclic NH band as a weakly pronounced doublet at 3077 and 3049 cm^{-1}. These values fall within the range (2950—3255 cm^{-1}) characteristic of the signals due to the NH bands in unsubstituted 1,2,3-triazoles[11] and their 1-oxides.[8] This band is absent from the IR spectra of compound **5** in AcOEt, MeCN, and $CHCl_3$ (3000—4000 cm^{-1}). Note that its structural analog, namely, 4-amino-5-nitro-1,2,3-triazole 1-oxide, exists in DMSO-d_6 in both forms (OH and NH), the N(2)H structure being dominant (^{14}N and ^{15}N NMR, NOESY).[8]

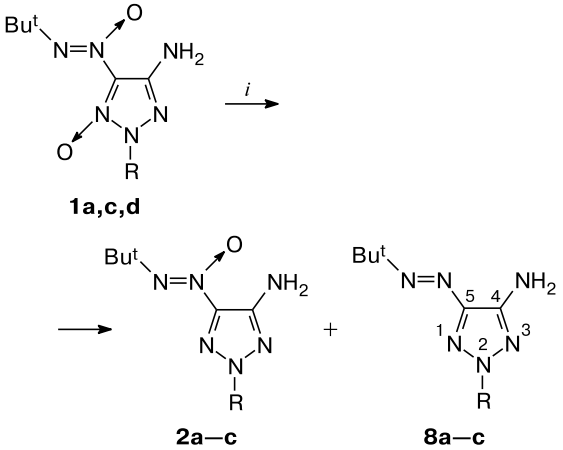
Reduction of triazole oxides 1a,c,d. Compounds **1a**,**c**,**d** were reduced with granulated Zn in EtOH/AcOH. In the reduction of compound **1d** (R = Bu^t), first the triazole oxide ring loses the oxygen atom to form triazole **2c** (Scheme 6). As the latter accumulates, it eliminates the O atom of the *tert*-butylazoxy fragment, thus becoming reduced to azo compound **8c**. Because of this, the yield of triazole **2c** is only 48%. For triazole oxides **1a**,**c** (R = Me and Pr^i), the rates of the conversion **2a**,**b** → **8a**,**b** are higher, so the yields of compounds **2a**,**b** are 30 and 23%, respectively. Note that these yields were achieved when the conversion of the starting triazole oxides **1** was incomplete.

Structure confirmation. The compounds obtained were studied by a number of physicochemical techniques, and their structures were confirmed. All the signals in their ^{1}H and ^{13}C NMR spectra were assigned, with consideration

Scheme 5



Scheme 6



R = Me (**1a**, **2a**, **8a**), Pr^i (**1c**, **2b**, **8b**), Bu^t (**1d**, **2c**, **8c**);
1a → **2a** + **8a**; **1c** → **2b** + **8b**; **1d** → **2c** + **8c**

i. EtOH/AcOH, Zn, 25 °C, 2 h. The yields are 30 (**2a**) and 30% (**8a**); 23 (**2b**) and 37% (**8b**); 48 (**2c**) and 30% (**8c**).

for the substantial broadening of the signal for the C atom bearing the azoxy group (Tables 2, 3). The location of the

Table 2. ^{1}H and ^{14}N NMR spectra of compounds **1**, **2**, and **5**—**8** (δ, *J*/Hz)[a]

Compound	^{1}H (*J*/Hz)			^{14}N ($\Delta\nu_{1/2}$/Hz)		
	$C\underline{Me}_3$ (s, 9 H)	NH_2[b] (s, 2 H)	R[c]	$\underline{N}(O)=NBu^t$	N(1)	N(2)[d]
1a[e]	1.47	5.1	3.85 (s, 3 H, Me)	−68 (75)	−88 (480)	—
1b	1.47	5.1	1.40 (t, 3 H, $CH_2\underline{Me}$, *J* = 7.3) 4.29 (m, 2 H, $C\underline{H}_2Me$, *J* = 7.3)	−67 (85)	−88 (470)	—
1c	1.48	5.0	1.42 (d, 6 H, $CH\underline{Me}_2$, *J* = 6.7) 5.19 (m, 1 H, $C\underline{H}Me_2$, *J* = 6.7)	−68 (80)	−88 (430)	—
1d	1.47	4.9	1.70 (s, 9 H, CMe_3)	−65 (75)	−85 (440)	—
1e	1.47	4.9	0.96 (t, 3 H, $CH_2CH_2CH_2\underline{Me}$, *J* = 7.3) 1.38 (m, 2 H, $CH_2CH_2C\underline{H}_2Me$, *J* = 7.3) 1.82 (m, 2 H, $CH_2C\underline{H}_2CH_2Me$, *J* = 7.3) 4.25 (t, 2 H, $C\underline{H}_2CH_2CH_2Me$, *J* = 7.3)	−67 (80)	−89 (360)	—
2a	1.48	5.0	4.04 (s, 3 H, Me)	−61 (90)	—	—
2b	1.48	5.0	1.53 (d, 6 H, $CH\underline{Me}_2$, *J* = 6.7) 4.65 (m, 1 H, $CHMe_2$, *J* = 6.7)	−58 (120)	—	−141
2c	1.47	4.6	1.62 (s, 3 H, CMe_3)	−59 (100)	—	−128
5[f]	1.39	5.9	13.7 (br.s, 1 H, OH)	−64 (150)	—	—
6[f]	1.41	6.0	4.22 (s, 3 H, OMe)	−65 (180)	—	—
6	1.47	5.0	4.32 (s, 3 H, OMe)	−66 (80)	—	—
7[f]	1.37	5.9	—	−63 (500)	—	—
8a	1.33	5.1	4.07 (s, 3 H, Me)	—	—	−150
8b	1.34	5.0	1.57 (d, 6 H, $CH\underline{Me}_2$, *J* = 6.7) 4.65 (m, 1 H, $C\underline{H}Me_2$, *J* = 6.7)	—	—	−135
8c	1.33	4.7	1.65 (s, 9 H, CMe_3)	—	—	−125

[a] In $CDCl_3$, unless otherwise specified.
[b] The signal for the NH_2 protons is broadened.
[c] R is the substituent on the heterocycle.
[d] For **2b**,**c**, $\Delta\nu_{1/2}$ ~1000 Hz; for **8a**—**c**, $\Delta\nu_{1/2}$ = 450—700 Hz. The chemical shifts are not cited if the spectrum of the compound contains no signal for the N(2) atom.
[e] The ^{15}N NMR spectrum of compound **1a**: 12.03 ($Bu^t\underline{N}$=N(O)), 88.02 (N(1), $^{3}J_{(N(1),Me)}$ = 1.83 Hz), 139 (N(3)), 165.5 (N(2), $^{2}J_{(N(2),Me)}$ = 2.11 Hz), 334.8 (NH_2, $^{1}J_{(NH_2,H)}$ = 86 Hz).
[f] In DMSO-d_6.

Table 3. ^{13}C NMR spectra of compounds **1**, **2**, and **5**—**8** (δ)[a]

Compound	^{13}C				
	$C(\underline{Me})_3$	$\underline{C}(Me)_3$	C(4)	C(5)[b]	R[c]
1a	25.9	60.0	142.8	122.1	34.9 (Me)
1b	26.0	59.9	142.8	122.2	12.3 ($CH_2\underline{Me}$); 43.3 ($\underline{C}H_2Me$)
1c	26.0	59.9	142.6	122.3	19.9 ($CH\underline{Me}_2$); 50.2 ($\underline{C}HMe_2$)
1d	26.1	59.9	141.4	123.2	27.0 ($C\underline{Me}_3$); 65.9 ($\underline{C}Me_3$)
1e	26.0	59.9	142.6	122.1	13.2 ($CH_2CH_2CH_2\underline{Me}$); 19.7 ($CH_2CH_2\underline{C}H_2Me$); 29.3($CH_2\underline{C}H_2CH_2Me$); 47.6 ($\underline{C}H_2CH_2CH_2Me$)
2a	26.0	59.2	145.5	137.7	42.3 (Me)
2b[d]	25.9	59.1	145.0	137.2	21.9 ($CH\underline{Me}_2$); 58.1 ($\underline{C}HMe_2$)
2c	26.0	59.1	144.6	137.3	29.0 ($C\underline{Me}_3$); 63.7 ($\underline{C}Me_3$)
5[e]	25.7	58.8	144.3	119.7	—
6[e]	25.9	59.3	146.0	118.7	68.7 (OMe)
6	26.0	59.7	145.3	119.6	68.2 (OMe)
7[e]	25.9	58.1	143.7	120.2	—
8a	27.3	67.3	143.2, 143.3		41.8 (Me)
8b[d]	27.3	67.1	142.7, 142.8		22.0 ($CH\underline{Me}_2$); 57.3 ($\underline{C}HMe_2$)
8c	27.3	67.1	142.5, 142.8		29.0 ($C\underline{Me}_3$); 62.8 ($\underline{C}Me_3$)

[a] In $CDCl_3$, unless otherwise specified.
[b] The signal for the C(5) atom bound to the *tert*-butylazoxy group is broadened.
[c] R is the substituent on the heterocycle.
[d] The signals were assigned using the 2D correlation experiment (^{13}C—^{1}H HSQC).
[e] In DMSO-d_6.

methyl group in the methylated derivatives of triazole oxide **5** was determined from 2D NMR experiments (^{1}H—^{15}N COSY).

The ^{14}N NMR spectra of 1,2,3-triazole 1-oxides **1a—e** show narrow signals at δ −68 to −65 ($\Delta\nu_{1/2}$ ~80 Hz; *cf.* Refs 1, 7) for the N-oxide nitrogen atom of the *tert*-butylazoxy group and broadened signals at δ −89 to −85 ($\Delta\nu_{1/2}$~500 Hz; *cf.* Ref. 12) for the N-oxide nitrogen atom of the triazole ring.

The ^{14}N NMR spectra of 1,2,3-triazoles **2a—c** contain signals at δ −61 to −58 ($Bu^tN\underline{N}O$) and broad signals at δ −141 to −128 (N(2), triazole ring). The broadened ($\Delta\nu_{1/2}$ = 1000—2000 Hz) signals at δ −390 to −330 relate to the amino group in both 1,2,3-triazole 1-oxides and 1,2,3-triazoles.

The IR spectra of all the compounds obtained show absorption bands due to an unsubstituted amino group.

To sum up, we developed the method for the synthesis of 2-alkyl-4-amino-5-(*tert*-butyl-*NNO*-azoxy)-2*H*-1,2,3-triazole 1-oxides **1a—e** by reactions of 3-amino-4-(*tert*-butyl-*NNO*-azoxy)furoxan with aliphatic amines. The reduction of compounds **1a**,**c**,**d** gave 2-alkyl-4-amino-5-(*tert*-butyl-*NNO*-azoxy)-2*H*-1,2,3-triazoles **2a—c** and 2-alkyl-4-amino-5-(*tert*-butyldiazenyl)-2*H*-1,2,3-triazoles **8a—c**.

Experimental

^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded on a Bruker DRX-500 instrument (500.13, 125.7, 36.14, and 50.70 MHz, respectively). Chemical shifts are referenced to $SiMe_4$ (^{1}H, ^{13}C) or $MeNO_2$ (^{14}N; high-field chemical shifts relative to this external standard have negative values). The ^{15}N NMR signals were acquired using the INEPT and ^{1}H—^{15}N COSY techniques. IR spectra were recorded on a Bruker ALPHA-T spectrometer. Mass spectra were measured on a Kratos MS-300 instrument (EI, 70 eV). The course of the reactions was monitored by TLC on Merck 60 F_{254} plates. For column chromatography, silica gel was used. 3-Amino-4-(*tert*-butyl-*NNO*-azoxy)furoxan (**3a**)[7] and a solution of diazomethane in Et_2O[13] were prepared according to known procedures.

Synthesis of 2-alkyl-4-amino-5-(*tert*-butyl-*NNO*-azoxy)-2*H*-1,2,3-triazole 1-oxides (general procedure). ***A.*** An appropriate amine hydrochloride $RNH_2 \cdot HCl$ (R = Me or Et; 2.1 mmol) and Na_2CO_3 (106 mg, 1 mmol) were added with stirring at 25 °C to furoxan **3a** (402 mg, 2 mmol) in MeOH (15 mL). The reaction mixture was stirred until the Na_2CO_3 was dissolved completely (~2 h) and kept in a sealed vessel for 24 h. Then the solvent was removed *in vacuo*, and the residue was purified by column chromatography with AcOEt—light petroleum (1 : 3) as an eluent. The yields of triazole *N*-oxides **1a,b** are given in Table 1.

B. An appropriate amine RNH_2 (R = Pr^i, Bu, or Bu^t) or its solution (R = Me) in MeOH (2—3 mL) was added at 25 °C to a stirred solution of furoxan **3a** (402 mg, 2 mmol) in MeOH or $CHCl_3$ (20 mL, see Table 1). The reaction mixture was stirred at 25 °C for a period of time specified in Table 1. The product was purified as described under ***A***. The yields of triazole *N*-oxides **1a**,**c—e** are given in Table 1.

C. An appropriate amine RNH_2 (R = Pr^i or Bu^t; 2 mmol) was added to a stirred solution of furoxan **3a** (402 mg, 2 mmol) in MeOH (15 mL). The reaction mixture was rapidly (in 2—3 min) heated to boiling (~64 °C) and refluxed for a period of time specified in Table 1. The product was purified as described under ***A***. The yields of triazole *N*-oxides **1c,d** are given in Table 1.

4-Amino-5-(*tert*-butyl-*NNO*-azoxy)-2-methyl-2*H*-1,2,3-triazole 1-oxide (1a) was obtained according to the methods ***A*** and ***B***. Yield 130 mg (30%), m.p. 75—79 °C. Found (%): C, 39.42; H, 6.63; N, 39.50. $C_7H_{14}N_6O_2$. Calculated (%): C, 39.25; H, 6.59; N, 39.23. IR (KBr), ν/cm^{-1}: 3474 s, 3445 s, 3317 s, 3297 s, 2999 w, 2974 s, 2929 m, 1617 s, 1564 s, 1503 s, 1477 s, 1454 s, 1435 s, 1360 m, 1343 s. MS, *m/z*: 214 $[M]^+$.

4-Amino-5-(*tert*-butyl-*NNO*-azoxy)-2-ethyl-2*H*-1,2,3-triazole 1-oxide (1b) was obtained according to the method ***A***. Yield 158 mg (34%), oil. Found (%): C, 42.31; H, 7.12; N, 36.94. $C_8H_{16}N_6O_2$. Calculated (%): C, 42.10; H, 7.07; N, 36.82. IR (thin film), ν/cm^{-1}: 3461 s, 3323 s, 2974 s, 2935 m, 2878 w, 1614 s, 1557 m, 1504 s, 1478 s, 1454 s, 1361 s, 1316 s. MS, *m/z*: 228 $[M]^+$.

4-Amino-5-(*tert*-butyl-*NNO*-azoxy)-2-isopropyl-2*H*-1,2,3-triazole 1-oxide (1c) was obtained according to the methods ***B*** and ***C***. Yield 166 mg (34%), crystals, m.p. 114—118 °C. Found (%): C, 44.60; H, 7.40; N, 35.01. $C_9H_{18}N_6O_2$. Calculated (%): C, 44.62; H, 7.49; N, 34.69. IR (KBr), ν/cm^{-1}: 3471 s, 3436 s, 3357 s, 3277 s, 3005 w, 2974 s, 2927 s, 2874 m, 1619 s, 1558 s, 1501 s, 1475 s, 1453 s, 1390 w, 1362 s, 1346 s. MS, *m/z*: 242 $[M]^+$.

4-Amino-2-*tert*-butyl-5-(*tert*-butyl-*NNO*-azoxy)-2*H*-1,2,3-triazole 1-oxide (1d) was obtained according to the methods ***B*** and ***C***. Yield 372 mg (73%) (***B***) and 409 mg (80%) (***C***), light yellow crystals, m.p. 141—145 °C (m.p. 145—146.5 °C from $CHCl_3$—light petroleum). Found (%): C, 46.70; H, 7.77; N, 32.98. $C_{10}H_{20}N_6O_2$. Calculated (%): C, 46.86; H, 7.87; N, 32.79. IR (KBr), ν/cm^{-1}: 3468 s, 3328 s, 3284 s, 2988 m, 2956 m, 2872 m, 1616 s, 1500 s, 1484 s, 1472 s, 1448 s. MS, *m/z*: 256 $[M]^+$.

4-Amino-2-butyl-5-(*tert*-butyl-*NNO*-azoxy)-2*H*-1,2,3-triazole 1-oxide (1e) was obtained according to the method ***B***. Yield 63 mg (12%). Found (%): C, 46.98; H, 7.80; N, 32.55. $C_{10}H_{20}N_6O_2$. Calculated (%): C, 46.86; H, 7.87; N, 32.79. IR (KBr), ν/cm^{-1}: 3461 s, 3327 s, 2964 s, 2934 s, 2875 s, 1614 s, 1558 s, 1504 s, 1478 s, 1460 s, 1361 s, 1343 s, 1316 s. MS, *m/z*: 256 $[M]^+$.

Reduction of 2-alkyl-4-amino-5-(*tert*-butyl-*NNO*-azoxy)-2*H*-1,2,3-triazole 1-oxides (1a,c,d) (general procedure). Acetic acid (2.4 g, 40 mmol) and granulated zinc (5 g, 75 mmol) were successively added at 25 °C to a stirred solution of triazole oxide **1** (2.4 mmol) in EtOH (16 mL). The reaction mixture was stirred at 25 °C for 2 h and filtered. The filter cake was washed with EtOH (2×10 mL). The filtrate was concentrated *in vacuo*. The residue was diluted with $CHCl_3$ (60 mL) and then with hexane (30 mL). The resulting precipitate of ZnOAc was filtered off, the filtrate was concentrated *in vacuo*, and the residue was separated by column chromatography with light petroleum—AcOEt (5 : 1) as an eluent.

Reduction of 4-amino-5-(*tert*-butyl-*NNO*-azoxy)-2-methyl-2*H*-1,2,3-triazole 1-oxide (1a) gave triazoles **2a** (142 mg, 30%) and **8a** (130 mg, 30%), with the starting compound **1a** (20 mg, 4%) being recovered.

4-Amino-5-(*tert*-butyl-*NNO*-azoxy)-2-methyl-2*H*-1,2,3-triazole (2a), m.p. 98—102 °C. Found (%): C, 42.50; H, 7.10; N, 42.37. $C_7H_{14}N_6O$. Calculated (%): C, 42.41; H, 7.12;

N, 42.40. IR (KBr), ν/cm^{-1}: 3478 s, 3355 s, 2968 s, 2929 m, 2873 w, 1611 s, 1559 m, 1459 m, 1438 s, 1400 s, 1361 s, 1342 m, 1306 s. MS, *m/z*: 198 [M]$^+$.

4-Amino-5-(*tert*-butyldiazenyl)-2-methyl-2*H*-1,2,3-triazole (8a), m.p. 54—55 °C. Found (%): C, 46.33; H, 7.76; N, 46.04. $C_7H_{14}N_6$. Calculated (%): C, 46.14; H, 7.74; N, 46.12. IR (KBr), ν/cm^{-1}: 3458 s, 3323 s, 2975 s, 2932 m, 2868 w, 1611 s, 1545 m, 1475 m, 1454 m, 1417 w, 1393 s, 1360 m, 1349 s, 1326 m. MS, *m/z*: 182 [M]$^+$.

Reduction of 4-amino-5-(*tert*-butyl-*NNO*-azoxy)-2-isopropyl-2*H*-1,2,3-triazole 1-oxide (1c) gave triazoles **2b** (126 mg, 23%) and **8b** (188 mg, 37%).

4-Amino-5-(*tert*-butyl-*NNO*-azoxy)-2-isopropyl-2*H*-1,2,3-triazole (2b), m.p. 96—99 °C. Found (%): C, 47.92; H, 8.10; N, 36.91. $C_9H_{18}N_6O$. Calculated (%): C, 47.77; H, 8.02; N, 37.14. IR (KBr), ν/cm^{-1}: 3439 s, 3355 s, 2978 s, 2932 s, 2877 w, 1614 s, 1559 s, 1488 s, 1470 s, 1440 s, 1405 m, 1392 m, 1374 m, 1361 s, 1319 s. MS, *m/z*: 226 [M]$^+$.

4-Amino-5-(*tert*-butyldiazenyl)-2-isopropyl-2*H*-1,2,3-triazole (8b), m.p. 95—97 °C. Found (%): C, 51.68; H, 8.52; N, 39.77. $C_9H_{18}N_6$. Calculated (%): C, 51.41; H, 8.63; N, 39.97. IR (KBr), ν/cm^{-1}: 3424 s, 3313 s, 2982 s, 2935 m, 2870 w, 1614 s, 1542 m, 1479 s, 1463 m. MS, *m/z*: 210 [M]$^+$.

Reduction of 4-amino-2-*tert*-butyl-5-(*tert*-butyl-*NNO*-azoxy)-2*H*-1,2,3-triazole 1-oxide (1d) gave triazoles **2c** (272 mg, 48%) and **8c** (162 mg, 30%).

4-Amino-2-*tert*-butyl-5-(*tert*-butyl-*NNO*-azoxy)-2*H*-1,2,3-triazole (2c), m.p. 161.5—162 °C. Found (%): C, 50.10; H, 8.33; N, 34.72. $C_{10}H_{20}N_6O$. Calculated (%): C, 49.98; H, 8.39; N, 34.97. IR (KBr), ν/cm^{-1}: 3488 s, 3366 s, 2985 s, 2963 s, 2934 m, 1613 s, 1556 w, 1482 m, 1464 m, 1439 s, 1373 s, 1362 s, 1342 m, 1330 s. MS, *m/z*: 240 [M]$^+$.

4-Amino-2-*tert*-butyl-5-(*tert*-butyldiazenyl)-2*H*-1,2,3-triazole (8c), m.p. 182—183 °C. Found (%): C, 53.62; H, 8.95; N, 37.46. $C_{10}H_{20}N_6$. Calculated (%): C, 53.55; H, 8.99; N, 37.47. IR (KBr), ν/cm^{-1}: 3474 s, 3343 s, 2973 s, 2964 s, 2870 m, 1604 s, 1476 s, 1465 s. MS, *m/z*: 224 [M]$^+$.

4-Amino-5-(*tert*-butyl-*NNO*-azoxy)-1-hydroxy-1*H*-1,2,3-triazole (5). ***A.*** Triazole oxide **1d** (1.280 g, 5 mmol) was dissolved with stirring at 25 °C in CF_3COOH (25 mL). The resulting solution was stirred for 15 min and concentrated *in vacuo*. The product was purified by column chromatography with AcOEt as an eluent. Yield 0.975 g (98%), m.p. 156—157 °C (decomp.).

B. Concentrated HCl (1 mL) was added at 25 °C to a stirred solution of triazole oxide **1d** (128 mg, 0.5 mmol) in AcOEt (5 mL). The resulting mixture was stirred for 30 min and evaporated to dryness *in vacuo*. The product was purified by column chromatography with AcOEt as an eluent. Yield 100 mg (100%). Found (%): C, 36.15; H, 6.09; N, 41.76. $C_6H_{12}N_6O_2$. Calculated (%): C, 36.00; H, 6.04; N, 41.98. IR (KBr), ν/cm^{-1}: 3410 s, 3284 s, 3077 s, 3049 s, 2980 s, 2963 s, 2919 s, 1657 s, 1572 s, 1510 s, 1472 s, 1446 s, 1405 s, 1341 s, 1322 s. MS, *m/z*: 200 [M]$^+$.

4-Amino-5-(*tert*-butyl-*NNO*-azoxy)-1-methoxy-1*H*-1,2,3-triazole (6). A solution of diazomethane in Et_2O was added at 5—10 °C to a stirred solution of hydroxytriazole **5** (100 mg, 0.5 mmol) in MeCN (10 mL) until the starting compound was consumed completely (TLC, $CHCl_3$). The solvents were removed *in vacuo*. The residue (88 mg) with m.p. 68—75 °C was purified by column chromatography with $CHCl_3$ as an eluent. The yield of compound **6** was 85 mg (80%), m.p. 76—79 °C. Found (%): C, 39.38; H, 6.57; N, 39.40. $C_7H_{14}N_6O_2$. Calculated (%): C, 39.25; H, 6.59; N, 39.23. IR (KBr), ν/cm^{-1}: 3428 s, 3302 s, 3014 m, 2979 s, 2947 s, 1638 s, 1579 s, 1486 s, 1468 s, 1446 s, 1361 s, 1308 s. MS, *m/z*: 214 [M]$^+$.

Sodium 4-amino-5-(*tert*-butyl-*NNO*-azoxy)-1*H*-1,2,3-triazol-1-olate (7). ***A.*** Sodium carbonate (212 mg, 2 mmol) was added at 25 °C to a stirred suspension of hydroxytriazole **5** (100 mg, 0.5 mmol) in MeOH (5 mL). The resulting mixture was stirred for 1 h, filtered to remove the excess Na_2CO_3, and concentrated *in vacuo*. The residue was passed through a short column with silica gel (AcOEt—MeOH (10 : 1) as an eluent). Concentration of the eluate gave sodium salt **7** (111 mg, 100%) as yellow crystals, m.p. 237—239.5 °C (decomp.).

B. A solution of NaOH (12 mg, 0.3 mmol) in MeOH (3 mL) was added at 25 °C to a stirred solution of hydroxytriazole **5** (57 mg, 0.3 mmol) in MeOH (5 mL). The resulting mixture was stirred for 5 min and concentrated *in vacuo*. The residue was passed through a short column with silica gel (AcOEt—MeOH (10 : 1) as an eluent). The yield of sodium salt **7** was 63 mg (100%). Found (%): C, 32.60; H, 5.01; N, 37.77. $C_6H_{11}N_6O_2Na$. Calculated (%): C, 32.54; H, 4.99; N, 37.83.

Alkylation of sodium 4-amino-5-(*tert*-butyl-*NNO*-azoxy)-1*H*-1,2,3-triazol-1-olate (7). Dimethyl sulfate (93 mg, 0.7 mmol) was added with stirring at 25 °C to sodium salt **7** (111 mg, 0.5 mmol) in acetone (6 mL). The reaction mixture was stirred for 4 h and concentrated *in vacuo*. Chloroform (15 mL) was added to the residue. The organic solution was washed with water (5 mL), dried with $MgSO_4$, and concentrated *in vacuo*. Separation of the residue (94 mg) by column chromatography with $CHCl_3$ as an eluent gave methoxytriazole **6** (48 mg, 45%) and triazole oxide **1a** (5 mg, 5%). Compounds **1a** and **6** are identical with those described above.

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