Benzo-1,2,3,4-tetrazine 1,3-Dioxides: Synthesis and NMR Study

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Benzo-1,2,3,4-tetrazine 1,3-dioxides (BTDOs) represent fairly stable high-nitrogen systems, incorporating two head-to-tail linked azoxy groups. The synthetic pathway to these heterocycles suggested the use of the *tert*-butyl-*NNO*-azoxy group as a building block, allowing the first azoxy group to be incorporated into the ring. The second azoxy group was added with the help of the oxodiazonium ion (–N=N=O$^+$) or its synthetic equivalent. This could be generated by two new methods. The first of these involved treatment of *N*-nitroamines with nitrating agents, and the second treatment of diazonium salts with peracids in the presence of a base. The proposed key stage in the tetrazine 1,3-bis(*N*-oxide) ring formation is the reaction between the oxodiazonium ion and the distal nitrogen atom of the *tert*-butyl-*NNO*-azoxy group, followed by elimination of the *tert*-butyl cation. The syntheses of bromo-BTDOs **3b**–**f** and nitro-BTDOs **4a**–**c** are described. The BTDOs were characterized by NMR, including ^{14}N and ^{15}N experiments.

Introduction

Cyclic compounds with several linked nitrogen atoms attract significant interest in the context of the stability of high-nitrogen systems[1] and in connection with the problem of heteroaromaticity. The 1,2,3,4-tetrazine (i.e., the six-membered aza-aromatic) ring system is one such compound. In contrast to tetrahydro-1,2,3,4-tetrazines[1] and cyclopenta-annulated 2-aryl-1,2,3,4-tetrazines,[2] thorough investigations of completely aromatic members of this class seem to be lacking. Compounds including the 1,2,3,4-tetrazine ring have been proposed as intermediates in a number of publications,[3] but the only 1,2,3,4-tetrazine to have had its structure unambiguously proven by X-ray analysis has been 2-phenyl[1,2,3]triazolo[4,5-*e*][1,2,3,4]tetrazine, synthesized by A. Ohsawa et al.[4] This compound was not stable, decomposing slowly at room temperature with elimination of nitrogen. 1,2,3,4-Tetrazine 1,3-dioxides (TDOs) were not known prior to our publications, but the first representatives of benzo-[5] and furazano-annulated[6] TDOs have now been described in preliminary form. The synthetic routes to these compounds included new ring-closure reactions. Here we describe the scope of these reactions and their plausible mechanisms. The structure of the parent compound, benzo-1,2,3,4-tetrazine 1,3-dioxide, has been confirmed by X-ray analysis.[7] The vibrational[8a,8b] and electronic absorption[8c] spectra of BTDOs have also been studied.

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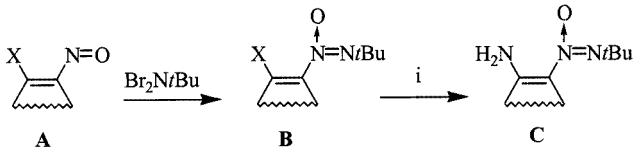
Results and Discussion

Starting Compounds

The starting compounds for the synthesis of benzo-1,2,3,4-tetrazine 1,3-dioxides (BTDOs) were anilines bearing the *tert*-butyl-*NNO*-azoxy group in the *ortho*-position[9,10] (**C**, Scheme 1). The key intermediates in their synthesis were compounds **B** (X = NO_2 or Hal) obtained by treatment of the appropriate nitrosobenzenes **A** with *N*,*N*-dibromo-*tert*-butylamine according to the Kovacic method.[11] Anilines **C** were obtained from **B** by reduction of the nitro group (X = NO_2) or by displacement of the halogen with ammonia (X = Hal).

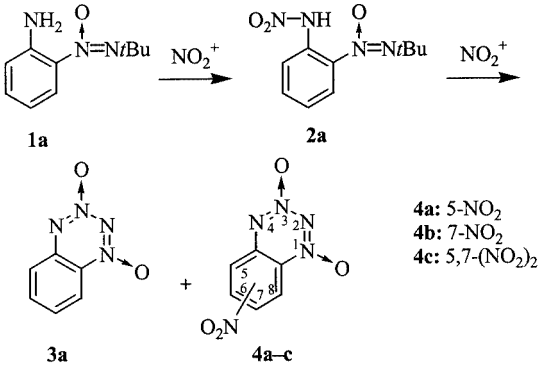


Scheme 1. Reagents: i, $SnCl_2$ (for X = NO_2) or NH_3 (for X = Hal)

Synthesis of BTDOs by the "Nitration" Method

Treatment of aniline **1a** with excess N_2O_5 in an organic solvent gave BTDO **3a**, together with the 5-nitro-, 7-nitro-, and 5,7-dinitro-BTDOs **4a**, **4b**, and **4c**, respectively (Scheme 2, Table 1). In the first stage of this reaction, *N*-nitroaniline **2** was formed, and this could be isolated when the reaction was carried out with 1 equiv. of N_2O_5.[12] It was shown by independent experimentation that BTDO **3a** was not nitrated to afford nitro BTDOs **4a**–**c** under similar

reaction conditions,[13] and so the nitration of the benzene ring of **2** must have preceded the cyclization. Thus, nitroamine **2** had undergone two competitive reactions, *C*-nitration and ring closure. The product ratio depended on the reaction conditions, particularly on the nitrating reagent and the solvent used. The highest yield of **3a** was achieved with N_2O_5 in CH_3NO_2 (Table 1), whereas the ring-nitrated BTDOs **4a−c** were predominant in CH_2Cl_2 or in trifluoroacetic acid. Nitration with NO_2BF_4 likewise resulted mainly in the ring-nitrated BTDOs.



Scheme 2

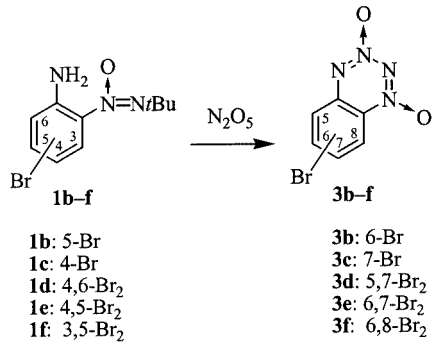
Table 1. The yields of BTDOs **3a** and **4a−c** obtained by treatment of **1a** with nitrating agents

Entry	Reagent	Solvent	Yield [%]			
			3a	**4a**	**4b**	**4c**
1	N_2O_5	$MeNO_2$	65	4	9	5
2	N_2O_5	MeCN	41	13	16	10
3[a]	N_2O_5	CH_2Cl_2	6	10	7	28
4[a]	N_2O_5	CF_3CO_2H	6	7	10	17
5[a]	NO_2BF_4	MeCN	3	8	27	21

[a] Yield determined by HPLC after workup of the reaction mixture.

Ring nitration might proceed through rearrangement of *N*-nitroamines in acidic media,[14] and/or by direct nitration of the ring. In any case, when treated with trifluoroacetic acid, *N*-nitroaniline **2a** yielded 2-(*tert*-butyl-*NNO*-azoxy)-4-nitroaniline and 2-(*tert*-butyl-*NNO*-azoxy)-6-nitroaniline in a 1:2 ratio.[12] Thus, to minimize ring nitration, strongly acidic conditions had to be avoided.

The cyclization of bromo-substituted 2-(*tert*-butylazoxy)-anilines **1b−f** also proceeded smoothly on treatment with N_2O_5 (Scheme 3). Good yields were obtained for 6- and 7-substituted BTDOs in which the bromine atoms were distant from the reacting moieties (Table 2). In contrast to the case of **1a**, only small amounts of the ring-nitrated BTDOs were formed. In the case of aniline **1d**, in which the *ortho*- and *para*-positions were occupied by bromine atoms, these by-products were not observed at all. For the preparation of bromo-BTDOs, CH_3CN was as a rule a preferable solvent to CH_3NO_2, owing to the ease of separation of the products, which precipitated from the reaction mixture at low temperatures.



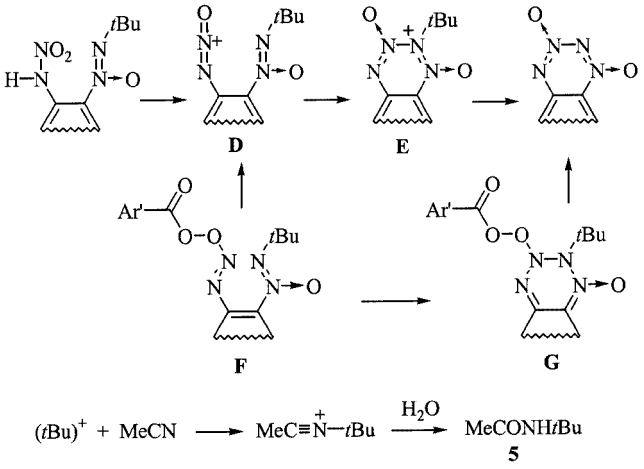
Scheme 3

Table 2. The yields of BTDOs **3a−f** obtained by the "nitration" and "oxidation" methods (in MeCN)

Method	Yield [%]					
	3a	**3b**	**3c**	**3d**	**3e**	**3f**
"Nitration"	41	76	62	53	72	45
"Oxidation"	70	84	51	52	70	37

Mechanism of the TDO Ring Formation

The formation of the TDO ring can be explained in terms of an ionic mechanism involving the formation of the intermediate oxodiazonium ion from the *N*-nitroamino group (Scheme 4, intermediate **D**). The electrophilic attack of this cation on the distal N atom of the *tert*-butylazoxy group should result in formation of the cyclic cation **E**, which would afford TDO after elimination of the *tert*-butyl cation. *N*-(*tert*-Butyl)acetamide (**5**) was observed after aqueous workup of the reaction mixture (80% yield) when the reaction was carried out in CH_3CN as a solvent. This amide could arise from capture of the *tert*-butyl cation by CH_3CN.

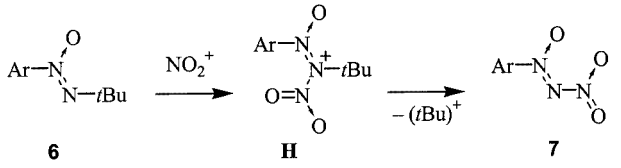


Scheme 4

There are two features of the proposed mechanism worthy of note. The first is the interaction of the azoxy

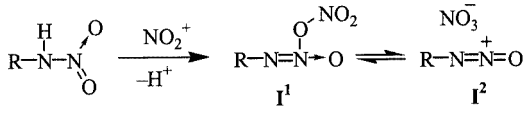
group with electrophiles, and the second is the formation of the hypothetical oxodiazonium ion.

The intramolecular coupling of the oxodiazonium ion with the *tert*-butylazoxy group is closely related to the intermolecular coupling of the nitronium ion with this group. The nitration of 1-aryl-2-(*tert*-butyl)diazene 1-oxides **6** with NO_2BF_4 or N_2O_5 resulted in 1-aryl-2-nitrodiazene 1-oxides **7**[15] (Scheme 5). The elimination of the *tert*-butyl cation from the intermediate **H** was very fast, but this intermediate was observed in some cases by NMR spectroscopy at low temperatures.[16]



Scheme 5

We could suggest the following reactions resulting in the formation of the oxodiazonium ion (Scheme 6). Treatment of the nitramine with a nitrating agent could afford *O*-nitrated covalent compound $\mathbf{I^1}$, which might exist in equilibrium with the ionic pair $\mathbf{I^2}$, in an equilibrium resembling the ionization of N_2O_5 in polar solvents. The protonation of $\mathbf{I^1}$ could facilitate the dissociation.



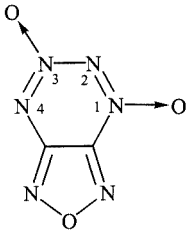
Scheme 6

Not much is known about oxodiazonium ions. These ions, generated from aliphatic *O*-acetylated *N*-nitroamines or *O*-acetyl-*N*-nitrosohydroxylamines, were proposed by E. White as intermediates as early as the 1960s,[17] but their only reaction was the elimination of N_2O with the formation of alkyl cations. Oxodiazonium ions bearing aromatic substituent should be more stable. To the best of our knowledge, two research groups have reported the assumed intermediate formation of these cations from *ortho*-*N*-nitroaminobenzonitriles in the synthesis of 1,2,3-benzotriazine 2-oxides.[18] The presence of the *ortho*-cyano group was necessary for the formation of the oxodiazonium ion from nitroamine by this method.

In our previous publications it was proposed that oxodiazonium ions were the intermediates in the transformation of *N*-nitroamines into nitroso compounds under action of an acid[15] and into nitro compounds under action of N_2O_5.[15] The oxodiazonium ion, generated by nitration of the amino group, was believed to be trapped by the neighboring *N*-methylamino group in the synthesis of annulated 1-methyl-1,2,3-triazole 2-oxide.[19] It should be noted that aliphatic *N*-nitroamines $R-NHNO_2$ afforded nitrates $R-ONO_2$ when treated with N_2O_5[20,21] or FNO_2,[22] and *O*-nitrated nitramines of the type $\mathbf{I^1}$ were proposed as intermediates in these reactions.[22] They were very unstable, in contrast to the fairly stable aliphatic *N*,*N*-dinitroamines (see ref.[22] and literature cited there), and were not isolated.

Oxodiazonium ions cannot only be generated from *N*-nitroamines by nitrating agents. We recently demonstrated that *N*-nitroamine **2a** gave rise to BTDO **4a** when treated with phosphoric anhydride or phosphorus pentachloride in CH_3CN as a solvent.[12] These reactions can be explained in terms of a mechanism involving *O*-phosphorylation of *N*-nitroamine.

Further arguments in favor of true formation of the oxodiazonium ions in the TDO ring-closure process were put forward in discussion of the synthesis of furazano-annulated TDO **8**.[6]

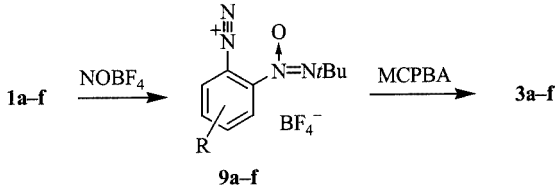


8

Synthesis of BTDOs by the "Oxidation" Method

It was reasonable to speculate that the precursors of oxodiazonium ions could be species of the **F** type (Scheme 4), which might be obtained by reaction between diazonium salts and anions of peracids.

Diazotization of anilines **1a–f** was carried out with $NOBF_4$. Diazonium salt **9a** was found to be fairly stable and was isolated in its pure state. Treatment of this salt with *meta*-chloroperbenzoic acid in the presence of pyridine at −15 °C in acetonitrile as a solvent afforded BTDO **3a** in good yield (Scheme 7). Pyridine was not oxidized under these conditions. The diazonium salts **9b–f**, bearing electron-withdrawing substituents, were not so stable, and underwent intramolecular cyclization at room temperature to give benzo-1,2,3,4-tetrazine 1-oxides.[23] When, however, bromo-substituted diazonium salts were produced at −15 °C and treated in situ with peracids, the appropriate BTDOs were obtained in yields similar to those obtained by the "nitration" method (Table 2). The advantages of the "oxidation" method lay in the absence of nitrated by-products.

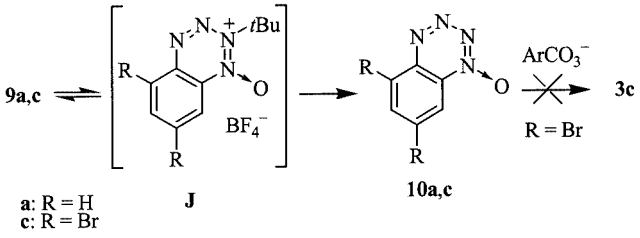


Scheme 7

The mechanism of BTDO formation might involve the formation of the intermediate azoperoxy compound **F**, followed by ionic dissociation to afford the oxodiazonium ion (Scheme 4). Ionic − but not radical − dissociation might be facilitated by intramolecular solvation of the oxodiazonium ion by the azoxy group.

However, it was found that the diazonium salt **9a** gave BTDO **3a** when treated with perbenzoic acid even when the reaction was carried out in aqueous acetonitrile in the presence of sodium acetate as a base. This cast some doubt on the intermediate formation of the oxodiazonium ion in this reaction, because this cation should react with water very rapidly. An alternative mechanism could be proposed, involving cyclization of **F** to afford the intermediate **G**, followed by ionic dissociation to afford the BTDO. The separation of *N*-*tert*-butylacetamide in 75% yield when the reaction was carried out in CH_3CN as solvent provided support for an ionic, and not a radical, mechanism for the reaction.

It might be speculated that the mechanism of BTDO formation could involve the cyclization of diazonium salt **9** to yield 1,2,3,4-tetrazine 1-oxide **10** via the intermediate salt **J** (Scheme 8). The oxidation of **10** could give rise to BTDO **3**.



Scheme 8

Indeed, cyclization of **9a** did take place, but the reaction needed a temperature of 50 °C to proceed.[23] The tetrazine 1-oxide **10a** was too unstable to be isolated at this temperature. Bromo-substituted diazonium salt **9c** was more reactive, and yielded **10c** at room temperature in 81% yield.[23] At this point, attempts were made to oxidize **10c** to **3c** with MCPBA/pyridine. It was shown that that reaction did not take place under these conditions, which were similar to those used for the formation of **3c** from diazonium salt **9c**. Thus, tetrazine 1-oxides could not have been the intermediates in the formation of the tetrazine 1,3-dioxide.

NMR Study of BTDOs

The full ^1H NMR and ^{13}C NMR assignments for the BTDOs **3a−f** and **4a−c** (see Exp. Sect.) were based on H,H COSY, C,H COSY, and SPT experiments, with the spectra being recorded both without proton decoupling and with selective proton decoupling. The broadening of C signals due to $^{13}C,^{14}N$ coupling allowed the C-8a carbon atom connected with the N-1 nitrogen atom of the tetrazine cycle and carbon atoms connected with the nitro groups to be assigned. This broadening was more pronounced in acetone or chloroform than in DMSO, due to the fact that ^{14}N signals are narrower in the former solvents. This broadening of ^{13}C signals can be suppressed by RF irradiation of the appropriate ^{14}N signal in a triple-resonance experiment ($(^{13}C\{^1H,^{14}N\text{-selective}\})$ proving the assignment. Increased intensities of the C(Br) signals due to the decrease in the relaxation time were also used for signal assignment. The values of the long-range coupling constants ^3J(5-H,C-8a) and ^3J(8-H,C-4a) were quite small (6.7 and 5.0 Hz, respectively). This observation may be helpful in the assignment of signals of substituted BTDOs.

The ^{14}N NMR spectrum of the parent BTDO **3a** showed two narrow peaks, each integrating to one nitrogen atom, that were attributable to the N-1 and N-3 nitrogen atoms,[24] and two very wide signals attributable to the N-2 and N-4 nitrogen atoms (Table 3). The selective polarization transfers (SPTs) from the 5-H and 8-H protons to the ^{15}N nucleus allowed assignment of the N-1 and N-4 signals, respectively. The ^{15}N NMR of **3a** (natural isotope content) showed four N signals (Table 4), and so all nitrogen signals of the TDO cycle had been assigned. ^{15}N NMR investigations of **4b** and **4c** based on natural isotope content also found four ring-nitrogen signals and the signals of the nitro groups in the typical region[25a] (Table 3).

Table 3. ^{14}N NMR assignments for BTDOs **3a−f** and **4a−c** in $[D_6]$acetone solutions

Compd.	δ(^{14}N)[a] Signal half-height widths [Hz] in parentheses		
	N-1	N-3	Other signals
3a[b]	−40 (20)	−48 (30)	−22 (400), N-2 −85 (400), N-4
3a[c]	−42 (400)		−21 (1000), N-2
3b[d]	−41 (100)	−48 (120)	
3c	−43 (35)	−48 (70)	
3d	−43 (45)	−49 (65)	
3e	−43 (35)	−47(50)	
3f	−42 (30)	−47 (50)	
4a	−41 (30)	−48 (45)	−18 (45), NO_2
4b	−40 (35)	−46 (50)	−18 (90), NO_2
4c	−41 (40)	−45 (60)	−23 (65), NO_2

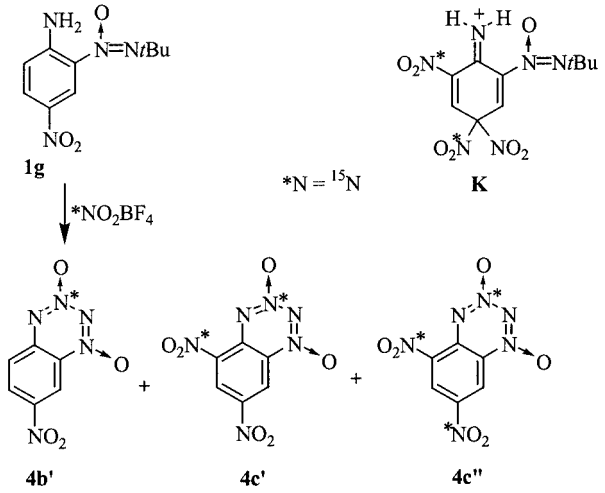
[a] Shifts are given from external $MeNO_2$. Negative values correspond to upfield shifts. [b] Ref.[5b] [c] $[D_6]$DMSO solution at 297 K. [d] $[D_6]$DMSO solution at 313 K.

Table 4. ^{15}N NMR assignments for BTDOs **3a**, **4b**, and **4c**

Compd.	Solvent	δ(^{15}N) [ppm][a]			
		N-1	N-2	N-3	N-4
3a[b]	$[D_6]$acetone	−41.0	−23.9	−48.7	−81.9
4b[c]	$[D_6]$DMSO	−40.3	−21.0	−46.3	−83.3
4c[d]	$[D_6]$DMSO	−41.2	−19.5	−45.8	−92.9
8[e]	$[D_6]$acetone	−52.7	8.0 t[f]	−43.9	−106.0

[a] Shifts are given from external $MeNO_2$. Negative values correspond to upfield shifts. [b] Ref.[5b] [c] For **4b**: δ = −16.9 ppm (NO_2); for **4b′**: δ = −46.3 ppm (N-3). [d] For **4c′** and **4c"**: δ = −45.5 ppm (N-3), −20.7 (5-NO_2), −21.4 (7-NO_2). [e] Ref.[6] [f] $^1J(^{14}N\text{-}1,^{15}N\text{-}2)$ = 20 Hz.

Further evidence of the above assignment was found on investigation of samples **4b′**, **4c′**, and **4c′′**, labeled with ^{15}N in position 3 (Scheme 9). These compounds were obtained by treatment of aniline **1g** with labeled $^{15}NO_2BF_4$.



Scheme 9

BTDO **4c′** bore the labeled nitro group in the 5-position. Unexpectedly, in addition to **4c′**, BTDO **4c′′** was also obtained, its nitro group in position 7 having been replaced with the labeled nitro group (the **4c′**/**4c′′** ratio was 3:1 on the basis of the integral intensities of ^{15}N signals). Evidently, exchange of the nitro groups[26] had taken place in *N*,4,6-trinitroaniline prior to cyclization through the intermediate cation **K** (see Scheme 2).

To summarize, the TDO cycle could easily be identified by ^{14}N NMR examination (see Table 3). All BTDOs investigated showed two signals in the $\delta = -40$ to -49 ppm region. These signals were fairly narrow in acetone or chloroform (signal half height width: 20−70 Hz). It was noteworthy that the N-1 signal was narrower than the N-3 signal in all cases investigated. In DMSO, the *N*-oxide signals were wide at room temperature and, as a rule, only one broad signal could be observed. To avoid the collapse of signals in this solvent, however, it was possible to record the spectra at elevated temperatures.

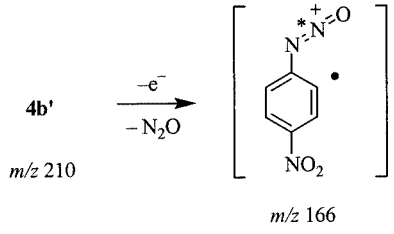
It is interesting to compare the ^{15}N chemical shifts of BTDOs with the chemical shifts of diazene oxides. The N-1 and N-3 signals were in the same region as the *N*-oxide N signal in azoxybenzene[25b] ($\delta = -54.0$ ppm) or in 1-phenyl-2-nitrodiazene 1-oxide[27] (**7**, Ar = Ph, $\delta = -45.5$ ppm). The N-2 signals of BTDOs differed little from the signals of the distal N atoms of diazene oxides with strongly electronegative substituents [e.g., for 2-nitro-1-phenyldiazene 1-oxide δ(N-2) = −34.0], but the N-4 atoms of BTDOs were much more shielded than the distal N atom of azoxybenzene ($\delta = -46.7$ ppm).[25b]

It was noteworthy that the chemical shift of N-3 in the furazano-annulated TDO **10**[6] was only slightly different from those of its counterpart in benzo-annulated compounds, whereas the N-1 and N-4 signals were shifted upfield and the N-2 signal exhibited a strong downfield shift (Table 4).

Thermal Stability of TDOs

All the BTDOs investigated were quite stable compounds, melting as a rule without decomposition in the 170−250 °C region. The increase in the stability of the tetrazine 1,3-dioxide ring relative to the parent tetrazine ring was due to the stabilizing effect of the oxygen atoms in the 1- and 3-positions. We were able to reason that this arrangement of oxygen atoms should be the most favorable. According to calculations, this cycle should be the thermodynamically most stable in comparison with 1,2,3,4-tetrazines bearing *N*-oxide oxygen atoms in other positions.[28] Tetrazine 1,3-dioxide, unlike tetrazine itself, tetrazine monooxides and tetrazine 2,3-dioxide cannot take part in ring-chain tautomerism. Finally, it cannot lose a thermodynamically stable N_2 molecule, again in contrast to tetrazine[4] or tetrazine 1,4-dioxide.[28] The loss of N_2O is not as favorable as the loss of N_2. Thus, tetrazine 1,3-dioxides differ strongly from the parent tetrazines and in fact represent a new high-nitrogen heterocyclic system.

All BTDOs synthesized gave their molecular ion peaks in the EI mass spectra. The characteristic feature of the BTDOs fragmentation was the stepwise loss of N_2O molecules, fragments $[M - N_2O]^+$ and $[M - 2\ N_2O]^+$ being observed. Study of the labeled ^{15}N BTDO **4b′** showed that the ^{15}N atom was retained in the molecule after the loss of the first N_2O molecule (Scheme 10). Thus, the $[M - N_2O]^+$ fragment bears a relatively stable oxodiazonium ion.



Scheme 10

In conclusion, two synthetic pathways to benzo-1,2,3,4-tetrazine 1,3-dioxides are described. The study of the chemical behavior of these compounds, including electrophilic and nucleophilic displacement at the benzene ring, is in progress.

Experimental Section

General: NMR spectra were recorded with a Bruker AM 300 instrument at 298 K; chemical shifts are in δ units downfield from internal TMS (^1H, ^{13}C) or external CH_3NO_2 (^{14}N, ^{15}N). ^1H and ^{13}C NMR spectra of BTDO **3a** were calculated by use of the program PANIC (Bruker) with an Aspect 3000 computer. The signs of small coupling constants were determined by calculation to obtain the best fit of experimental and calculated spectra. ^1H RMS of calculations was 0.005; ^{13}C RMS was not worse then 0.1. MS data were obtained at 70 eV by electron impact. Melting points are

uncorrected. Anilines **1a−d** and **1f**,[9] **1e**,[10] and **1g**[12] were synthesized by published procedures. Labeled $^{15}NO_2BF_4$ was prepared from [^{15}N]nitric acid (96 atom% ^{15}N) by a literature procedure.[29]

Warning: *The compounds described in this paper are potentially explosive and appropriate precautions should be taken in their handling. At the same time, the toxicity of BTDOs is not high (e.g., for 7-NO_2-BTDO **4b**, LD_{50} is no more than 50 mg/kg for mice).*

Materials: Dinitrogen pentoxide was prepared by a literature procedure[30] from concd. HNO_3 and P_4O_{10} in a flow of dry argon and purified from N_2O_4 by repeated evacuation (15 Torr) at 0 °C until the material became free-flowing and the color of the vapor above the crystals had changed from red-brown to pale yellow. Traces of N_2O_4 in the material obtained in this way had no unfavorable effect on the reactions described below.

Preparation of Benzo-1,2,3,4-tetrazine 1,3-Dioxides (BTDOs) 3a and 4a−c by the "Nitration" Method. Table 1, **Entry 1:** A solution of aniline **1a** (0.23 g, 1.5 mmol) in nitromethane (6 mL) was added drop by drop over a period of 10 min to a stirred and cooled (−15 °C) suspension of N_2O_5 (0.65 g, 6 mmol) in dry nitromethane (20 mL). The reaction mixture was then gradually brought to 10 °C over 10 min. The solution was concentrated in vacuo to ca. 90%, and the precipitate was dissolved in CH_2Cl_2 and washed with aqueous $NaHCO_3$ solution and with water. The solvent was evaporated and the residue was chromatographed (silica gel; eluent hexane/EtOAc, 4:1). The yellow spots corresponding to BTDOs on chromatograms were distinguished by treatment with vapors of ammonia. BTDO **3a** did not change in color. The spots of **4a**, **4b**, and **4c** became orange, dark blue, and red, respectively. **Entries 2 and 3:** The reaction was carried out similarly in MeCN and CH_2Cl_2 as solvents. **Entry 4:** The solution of N_2O_5 was prepared in situ by dropwise addition of trifluoroacetic anhydride (0.42 mL, 3 mmol) to stirred HNO_3 (ρ = 1.5 g·cm^{-3}, 0.25 mL, 6 mmol) at 0 to −5 °C.[31] To this solution, a solution of **1a** (0.2 g, 1.0 mmol) in trifluoroacetic acid (1 mL) was added dropwise at −20 °C whilst stirring. After warming to 0 °C, the reaction mixture was poured into ice/water. The mixture was then neutralized with aqueous NaOH solution and extracted with EtOAc. **Entry 5:** NO_2BF_4 (0.40 g, 3.01 mmol) was added to a stirred and cooled (−30 °C) solution of **1a** (0.20 g, 1.03 mmol) in dry CH_3CN (15 mL). After 15 min of stirring at −30 °C, the temperature was brought to 20 °C and the reaction mixture was worked up as described above.

Benzo-1,2,3,4-tetrazine 1,3-Dioxide BTDO (3a): Yellow crystals, m.p. 170−172 °C. Tables 5 and 6. ^{13}C NMR ([D$_6$]DMSO): δ = 118.9 (C-8), 124.2 (C-5), 128.0 (C-8a), 131.8 (C-7), 138.4 (C-6), 143.3 (C-4a). IR (KBr):[8a,8b] $\tilde{\nu}$ = 1497 and 1402 [N_4O_2 fragment] cm^{-1}. MS (70 eV): *m/z* (%) = 164 (25) [M$^+$], 120 (11) [M$^+$ − N_2O], 90 (23), 76 (100) [M$^+$ − 2 N_2O]. $C_6H_4N_4O_2$ (164.1): calcd. C 43.91, H 2.46, N 34.14; found C 43.88, H 2.50, N 34.00.

Table 5. ^{1}H NMR assignments for BTDO **3a**

Proton	δ_H [D$_6$]acetone[a]	δ_H [D$_6$]DMSO	*J* [Hz] [D$_6$]acetone
5-H	7.92 m	7.97 d	$^3J(5,6)$ = 8.5
6-H	8.18 m	8.16 td	$^3J(6,7)$ = 7.1
7-H	7.91 m	7.88 td	$^3J(7,8)$ = 8.6
			$^4J(7,5)$ = 1.3
8-H	8.35 m	8.31 d	$^4J(8,6)$ = 1.3
			$^5J(8,5)$ = 0.6

[a] Ref.[5b]

Table 6. ^{13}C NMR assignments for BTDO **3a** in [D$_6$]acetone solution (ref.[5b])

Carbon	δ_C	$J_{C,H}$ [Hz] 5-H	6-H	7-H	8-H
C-4a	144.7	^2J = 1.5	^3J = 10.2	^4J = 0	^3J = 5.0
C-5	125.2	^1J = 171	^2J = 1.5	^3J = 7.6	^4J = −1.3
C-6	139.2	^2J = 0.5	^1J = 166	^2J = 1.7	^3J = 8.7
C-7	132.3	^3J = 8.7	^2J = 1.2	^1J = 169	^2J = −0.3
C-8	119.9	^4J = −1.3	^3J = 7.8	^2J = 1.9	^1J = 174
C-8a	129.0	^3J = 6.7	^4J = 1.5	^3J = 10.5	^2J = 2.6

5-Nitrobenzo-1,2,3,4-tetrazine 1,3-Dioxide (4a): Yellow crystals, m.p. 193−195 °C. ^{1}H NMR ([D$_6$]acetone): δ = 8.09 (dd, *J* = 8.7, 7.8 Hz, 1 H, 7-H), 8.68 (dd, *J* = 8.7, 1.2 Hz, 1 H, 8-H), 8.72 (dd, *J* = 7.8, 1.2 Hz, 1 H, 6-H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 124.5 (C-8, ^1J = 176.3, $^3J_{6\text{-H}}$ = 7.8, $^2J_{7\text{-H}}$ = 1.9 Hz), 129.8 (C-8a, $^3J_{7\text{-H}}$ = 11.1, $^2J_{8\text{-H}}$ = 2.5 $^4J_{6\text{-H}}$ = 1.2 Hz), 131.1 (C-7, ^1J = 174.5 Hz), 133.7 (C-6, ^1J = 172.6, $^3J_{8\text{-H}}$ = 8.9, $^2J_{7\text{-H}}$ = 2.3 Hz), 138.1 (C-4a, $^3J_{6\text{-H}}$ = 7.3, $^3J_{8\text{-H}}$ = 5.4, $^4J_{7\text{-H}}$ = 1.5 Hz), 142.7 br. (C-5, $^3J_{7\text{-H}}$ = 7.9, $^2J_{6\text{-H}}$ = 3.6, $^4J_{8\text{-H}}$ = 1.7 Hz) ppm. IR (KBr):[8a,8b] $\tilde{\nu}$ = 1507 and 1428 (N_4O_2 *syn* and *ansyn*), 1552 and 1350 (NO_2 *as* and *s*) cm^{-1}. MS (70 eV): *m/z* = 209 [M$^+$]. $C_6H_3N_5O_4$ (209.1): calcd. C 34.46, H 1.45, N 33.49; found C 34.33, H 1.47, N 33.29.

7-Nitrobenzo-1,2,3,4-tetrazine 1,3-Dioxide (4b): Yellow crystals, m.p. 166−168 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 8.21 (d, *J* = 9.0 Hz, 1 H, 5-H), 8.82 (dd, 1 H, 6-H), 8.93 (d, *J* = 2.5 Hz, 1 H, 8-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 115.4 (C-8, ^1J = 179.8 Hz), 126.4 (C-5, ^1J = 175.7 Hz), 128.1 (C-8a), 131.9 (C-6, ^1J = 175.3, ^3J = 3.8 Hz), 146.0 (C-4a, $^3J_{6\text{-H}}$ = 7.5, $^3J_{8\text{-H}}$ = 5.0 Hz), 147.6 (C-7, ^3J = 10.0, ^2J = 2.0 Hz) ppm. IR (KBr):[8a,8b] $\tilde{\nu}$ = 1517 and 1431 (N_4O_2 *syn* and *ansyn*), 1540 and 1345 (NO_2 *as* and *s*) cm^{-1}. MS (70 eV): *m/z* (%) = 209 (100) [M$^+$], 165 (57) [M$^+$ − N_2O], 121 (35) [M$^+$ − 2 N_2O], 105 (30). $C_6H_3N_5O_4$ (209.1): calcd. C 34.46, H 1.45, N 33.49; found C 34.52, H 1.48, N 33.38.

5,7-Dinitrobenzo-1,2,3,4-tetrazine 1,3-Dioxide (4c): Yellow crystals, m.p. 209−211 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 9.17 (d, *J* = 2.6, 1 H, 8-H), 9.48 (d, 1 H, 6-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 119.1 (C-8, ^1J = 180.8, 127.5 (C-6, ^1J = 178.5, ^3J = 4.7 Hz), 129.0 (br., C-8a), 139.6 (C-4a, $^3J_{6\text{-H}}$ = 7.5, $^3J_{8\text{-H}}$ = 6.6 Hz), 141.2 (C-5, ^2J = ^4J = 5.0 Hz), 146.0 (C-7, $^2J_{6\text{-H}}$ = $^2J_{8\text{-H}}$ = 5.0 Hz) ppm. IR (KBr):[8a,8b] $\tilde{\nu}$ = 1520 and 1432 (N_4O_2 *syn* and *ansyn*), 1548 and 1342 (NO_2 *as* and *s*) cm^{-1}. MS (70 eV): *m/z* = 254 [M$^+$]. $C_6H_2N_6O_6$ (254.1): calcd. C 28.36, H 0.79, N 33.07; found C 28.42, H 0.79, N 32.85.

Isolation of *N-tert*-Butylacetamide (5): The treatment of **1a** with N_2O_5 was carried out in MeCN as solvent as described above. After neutralization with saturated aqueous Na_2CO_3, the reaction solvents were evaporated to dryness in vacuo. The organic compounds were extracted with acetone. The ^{1}H NMR analysis showed *N-tert*-butylacetamide (yield 80%) and BTDOs **3a** and **4a−c** (overall yield 82%). The solution was concentrated and the residue was sublimed in vacuo to give pure *N-tert*-butylacetamide, m.p. 96−97 °C (ref.[32] 96−97 °C), identical with an authentic sample. MS (70 eV): *m/z* = 115 [M$^+$].

General Procedure for the Preparation of Benzo-1,2,3,4-tetrazine 1,3-Dioxides (BTDOs) 3b−f by the "Nitration" Method: A solution of aniline **1** (5 mmol) in dry CH_3CN (15 mL) was added dropwise over a period of 10 min to a stirred and cooled (−20 °C) suspension of N_2O_5 (2.16 g, 20 mmol) in dry CH_3CN (20 mL), and the reac-

tion mixture was gradually brought to 0 °C. After stirring for 10 min at this temperature, the reaction mixture was cooled to −25 to −30 °C. The precipitate was then filtered off and washed with a small amount of MeOH to give the practically pure BTDO as yellow crystals. The filtrate was poured into ice/water and extracted with CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$ solution and with water, and then dried ($MgSO_4$). The solvent was removed in vacuo. The residue was purified by chromatography on silica gel (eluent benzene) to give an additional quantity of BTDO **7** (see Table 2).

6-Bromobenzo-1,2,3,4-tetrazine 1,3-Dioxide (3b): Yellow crystals, m.p. 196−197 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 7.97 (dd, 1 H, 7-H), 8.19 (d, J = 9.0 Hz, 1 H, 8-H), 8.24 (d, J = 1.8 Hz, 1 H, 5-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 120.6 (C-8), 126.2 (C-5, ^1J = 176.4, $^3J_{7\text{-H}}$ = 5.2, $^4J_{8\text{-H}}$ = 1.2 Hz), 127.2 br. (C-8a), 132.3 (C-6, $^3J_{8\text{-H}}$ = 12.4, $^2J_{7\text{-H}}$ = 4.1, $^2J_{5\text{-H}}$ = 2.0 Hz), 134.5 (C-7, ^1J = 176.5, $^3J_{5\text{-H}}$ = 6.2, $^2J_{8\text{-H}}$ = 1.0 Hz), 144.0 (C-4a, $^3J_{8\text{-H}}$ = 5.7, $^2J_{5\text{-H}}$ = 2.0 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1508, 1420 cm^{-1}. MS (70 eV): *m*/*z* (ratio): 242, 244 (1:1) [M$^+$]. $C_6H_3BrN_4O_2$ (243.0): calcd. C 29.65, H 1.24, Br 32.88, N 23.05; found C 29.71, H 1.20, Br 32.71, N 22.89.

7-Bromobenzo-1,2,3,4-tetrazine 1,3-Dioxide (3c): Yellow crystals, m.p. 220−221 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 7.90 (d, J = 8.9 Hz, 1 H, 5-H), 8.28 (dd, 1 H, 6-H), 8.51 (d, J = 1.8 Hz, 1 H, 8-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 121.0 (C-8), 124.4 (C-7), 126.0 (C-5), 128.7 br. (C-8a), 141.3 (C-6), 142.5 (C-4a) ppm. IR (KBr): $\tilde{\nu}$ = 1508, 1415 cm^{-1}. MS (70 eV): *m*/*z* (ratio): 242, 244 (1: 1) [M$^+$]. $C_6H_3BrN_4O_2$ (243.0): calcd. C 29.65, H 1.24, Br 32.88, N 23.05; found C 29.60, H 1.24, Br 32.76, N 22.93.

5,7-Dibromobenzo-1,2,3,4-tetrazine 1,3-Dioxide (3d): Yellow crystals, m.p. 204−208 °C (dec.). ^{1}H NMR ([D$_6$]acetone): δ = 8.57 (d, 1 H), 8.62 (d, Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 119.9 (C-5, $^2J_{6\text{-H}}$ = 4.5, $^4J_{8\text{-H}}$ = 1.9 Hz), 122.0 (C-8, ^1J = 179.9, $^3J_{6\text{-H}}$ = 5.8 Hz), 124.7 (C-7, $^2J_{6\text{-H}}$ = $^2J_{8\text{-H}}$ = 4.5 Hz), 130.7 br. (C-8a), 142.7 (C-4a, $^3J_{6\text{-H}}$ = 8.1, $^3J_{8\text{-H}}$ = 5.1 Hz), 144.7 (C-6, ^1J = 176, $^3J_{8\text{-H}}$ = 6.5 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1498, 1405 cm^{-1}. MS (70 eV): *m*/*z* (ratio): 320, 322, 324 (1:2:1) [M$^+$]. $C_6H_2Br_2N_4O_2$ (321.9): calcd. C 22.39, H 0.63, Br 49.64, N 17.40; found C 22.43, H 0.60, Br 49.70, N 17.31.

6,7-Dibromobenzo-1,2,3,4-tetrazine 1,3-Dioxide (3e): Yellow crystals, m.p. 252−254 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 8.56 (s, 1 H, 5-H), 8.89 (s, 1 H, 8-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 123.1 (C-8), 127.3 (C-7, $^3J_{5\text{-H}}$ = 9.5, $^2J_{8\text{-H}}$ = 4.4 Hz), 127.9 br. (C-8a, $^3J_{5\text{-H}}$ = 7.4, $J_{8\text{-H}}$ = 3.4 Hz), 128.5 (C-5), 135.4 (C-6, $^3J_{8\text{-H}}$ = 9.6, $^2J_{5\text{-H}}$ = 4.4 Hz), 142.8 (C-4a, $^3J_{8\text{-H}}$ = 5.9, ^2J = 2.1 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1495, 1430 cm^{-1}. MS (70 eV): *m*/*z* (ratio): 320, 322, 324 (1:2:1) [M$^+$]. $C_6H_2Br_2N_4O_2$ (321.9): calcd. C 22.39, H 0.63, Br 49.64, N 17.40; found C 22.61, H 0.64, Br 49.81, N 17.27.

6,8-Dibromobenzo-1,2,3,4-tetrazine 1,3-Dioxide (3f): Yellow crystals, m.p. 213−215 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 8.29 (d, J = 2.0, 1 H, 5-H), 8.37 (d, 1 H, 7-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 114.0 (C-8, $^2J_{7\text{-H}}$ = 4, $^4J_{5\text{-H}}$ = 2 Hz), 126.3 (C-5, ^1J = 178.3, $^3J_{7\text{-H}}$ = 6.3 Hz), 126.8 br. (C-8a, ^3J = 8.8, ^3J = 6.7 Hz), 131.2 (C-6, $^2J_{7\text{-H}}$ = $^2J_{5\text{-H}}$ = 2.0 Hz), 139.1 (C-7, ^1J = 178.7, $^3J_{5\text{-H}}$ = 6.4 Hz), 146.4 (C-4a, ^2J = ^4J = 1.0 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1518, 1412 cm^{-1}. MS (70 eV): *m*/*z* (ratio): 320, 322, 324 (1:2:1) [M$^+$]. $C_6H_2Br_2N_4O_2$ (321.9): calcd. C 22.39, H 0.63, Br 49.64, N 17.40; found C 22.31, H 0.61, Br 49.76, N 17.30.

General Procedure for the Preparation of Benzo-1,2,3,4-tetrazine 1,3-Dioxides (BTDOs) 3a−f by the "Oxidation" Method: A solution of aniline **1** (1.43 mmol) in dry CH_3CN (5 mL) was added dropwise to a stirred and cooled (−15 °C) suspension of $NOBF_4$ (0.2 g, 1.71 mmol) in dry CH_3CN (15 mL) over a period of 10 min. The reaction mixture was stirred for an additional 10 min at that temperature, and *m*-chloroperbenzoic acid (2.14 mmol) was then added, followed by a solution of pyridine (0.28 g, 3.6 mmol) in MeCN (3 mL). The solution was allowed to warm to room temperature for 15 min and then poured into water and extracted with CH_2Cl_2. The extract was washed with 5% aqueous NaOH and with 5% aqueous HCl solutions and then with water. The organic layer was dried ($MgSO_4$), and the solvent was evaporated in vacuo. Crude products were purified by chromatography on silica gel (eluent benzene) (see Table 2). The BTDOs obtained were identical to BTDOs prepared by the "nitration" method.

2-(*tert*-Butyl-*NNO*-azoxy)phenyldiazonium Tetrafluoroborate (9a): A solution of aniline **1a** (1.0 g, 5.18 mmol) in dry CH_3CN (3 mL) was added dropwise to a stirred and cooled (−15 °C) suspension of $NOBF_4$ (0.66 g, 5.6 mmol) in dry CH_3CN (10 mL). The reaction mixture was allowed to warm to 10 °C and stirred at this temperature until the $NOBF_4$ had dissolved. After an additional 5 min, the solution was concentrated in vacuo to near dryness, and dry Et_2O (25 mL) was added. The precipitate was filtered off, washed with Et_2O (5 mL) and pentane (5 mL), and then dried in vacuo to give 1.41 g of **9a** (93%) as white crystals. ^{1}H NMR ([D$_6$]acetone): δ = 1.53 (s, 9 H, *t*Bu), 8.25 (t, J = 8.2 Hz, 1 H, 5-H), 8.52 (t, J = 8.2 Hz, 1 H, 4-H), 8.70 (d, J = 8.2 Hz, 1 H, 3-H), 8.99 (d, J = 8.2 Hz, 1 H, 6-H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 25.4 (CH_3), 61.9 (*C*Me$_3$), 110.9 (C-1), 127.1 (C-3), 134.8 (C-5), 137.1 (C-6), 143.1 (C-4), 146.8 br. (C-2). The assignment of ^{1}H NMR and ^{13}C NMR signals was achieved by selective decoupling, SPT, C,COSY, and ^{13}C{^{14}N} experiments. ^{14}N NMR ([D$_6$]acetone): δ = −66 ($\Delta\nu_{1/2}$ = 85 Hz) (N→O), −154 ($\Delta\nu_{1/2}$ = 240 Hz) (N≡N) ppm. ^{15}N NMR, INEPT ([D$_6$]acetone): δ = −6.9 (=N-*t*Bu) ppm. IR (KBr): $\tilde{\nu}$ = 2300 cm^{-1}. $C_{10}H_{13}BF_4N_4O$ (292.0): calcd. C 41.13, H 4.49, N 19.18; found C 41.27, H 4.38, N 18.93.

Preparation of BTDO 3a by the "Oxidation" Method: A solution of AcONa (0.57 g, 7.0 mmol) in H_2O (15 mL) was added to a stirred and cooled (0 °C) solution of diazonium salt **9a** (0.98 g, 3.36 mmol) and perbenzoic acid (6.7 mmol) in MeCN (20 mL). The reaction mixture was stirred for 15 min at 0−3 °C. A solution of NaOH (1.5 g) in H_2O (5 mL) was then added, and the reaction mixture was extracted with Et_2O (3 × 25 mL). The extract was washed with concd. aqueous NaOH solution and with water, and then dried ($MgSO_4$). The solution was concentrated to dryness and washed with hot hexane (15 mL). The residue was purified by column chromatography (silica gel, eluent $CHCl_3$) to give **3a** (0.40 g, 72%) as yellow solid, identical with previously obtained material.

Isolation of *N*-*tert*-Butylacetamide (5): Treatment of diazonium salt **9a** with perbenzoic acid was carried out as described above. The reaction solvents were evaporated to dryness in vacuo. The ^{1}H NMR analysis showed *N*-*tert*-butylacetamide (yield 75%) and BTDO **3a** (yield 85%). Workup of the reaction mixture and sublimation gave pure *N*-*tert*-butylacetamide, m.p. 96−97 °C, identical with an authentic sample.

Preparation of ^{15}N-Labeled BTDOs 4b′, 4c′, and 4c′′. Treatment of 1g with $^{15}NO_2BF_4$: ^{15}N-Labeled (96%) nitronium tetrafluoroborate (0.40 g, 3.01 mmol) was added to a stirred and cooled (−20 °C) solution of aniline **1g** (0.24 g, 1.0 mmol) in dry CH_3CN (10 mL). After the mixture had been stirred for 30 min at room temperature, the solvent was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with cold water (12 mL). The organic layer was concentrated to a volume of 25 mL, filtered through a silica gel pad (eluent CH_2Cl_2), and chromatographed

(silica gel, eluent benzene) to give **4b′** (0.055 g, 26%) and a mixture of **4c′** and **4c′′** (0.17 g, 63%).

BTDO 4b′: ^{1}H NMR ([D$_6$]DMSO): ^5J(8-H,^{15}N-3) = 1.2 Hz. ^{13}C NMR ([D$_6$]DMSO): ^3J(^{13}C-5,^{15}N-3) = 5.0 Hz. MS (70 eV): *m*/*z* (%) = 210 (100) [M$^+$], 166 (60) [M$^+$ − N$_2$O], 121 (41) [M$^+$ − N$_2$O − ^{15}NNO], 105 (25).

BTDO 4c′: ^{1}H NMR ([D$_6$]DMSO): ^3J(6-H,^{15}N$_{5\text{-nitro}}$) = 3, ^5J(8-H,^{15}N-3) = 1 Hz. ^{13}C NMR ([D$_6$]DMSO): ^1J(^{13}C-5,^{15}N$_{5\text{-nitro}}$) = 19, ^3J(^{13}C-5,^{15}N-3) = 5.0, ^2J(^{13}C-6,^{15}N$_{5\text{-nitro}}$) = 2.0, ^3J(^{13}C-7,^{15}N$_{5\text{-nitro}}$) = 3.0, ^4J(^{13}C-8,^{15}N$_{5\text{-nitro}}$) = 3.0 Hz.

BTDO 4c′′: ^{1}H NMR ([D$_6$]DMSO): ^3J(6-H,^{15}N$_{7\text{-nitro}}$) = ^3J(8-H,^{15}N$_{7\text{-nitro}}$) = 2 Hz (besides that of **4c′**). ^{13}C NMR ([D$_6$]DMSO): ^1J(^{13}C-7,^{15}N$_{7\text{-nitro}}$) = 18 Hz (besides that of **4c′**).

[1] F. R. Benson, *The High Nitrogen Compounds*, Wiley, New York, **1984**.

[2] P. J. Mackert, K. Hafner, N. Nimmerfroh, K. Banert, *Chem. Ber.* **1994**, *127*, 1479−1488, and references cited therein.

[3] [3a] J. Nakayama, T. Segiri, R. Ohya, M. Hoshino, *J. Chem. Soc., Chem. Commun.* **1980**, 791−792. [3b] S.-J. Chang, *Synth. Commun.* **1982**, *12*, 673−680. [3c] H. Meier, *Synthesis* **1972**, *5*, 235−253. [3d] T. Nakazawa, M. Kodama, S. Kinoshita, I. Murata, *Tetrahedron Lett.* **1985**, *26*, 335−338. [3e] S. Czernecki, J.-M. Valery, *Carbohydr. Chem.* **1986**, *5*, 235−240.

[4] T. Kaihoh, T. Itoh, K. Yamaguchi, A. Ohsawa, *J. Chem. Soc., Perkin Trans. 1* **1991**, 2045−2048.

[5] [5a] A. M. Churakov, S. L. Ioffe, Yu. A. Strelenko, V. A. Tartakovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 718−719 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1990**, *39*, 639−640). [5b] A. M. Churakov, S. L. Ioffe, V. A. Tartakovsky, *Mendeleev Commun.* **1991**, 101−102.

[6] A. M. Churakov, S. L. Ioffe, V. A. Tartakovsky, *Mendeleev Commun.* **1995**, 227−228.

[7] K. Yamaguchi, H. Takahashi, T. Kaihoh, T. Itoh, M. Okada, K. Nagata, G. Matsumura, A. Ohsawa, *Acta Crystallogr., Sect. C* **1992**, *48*, 1237−1239.

[8] [8a] K. I. Rezchikova, A. M. Churakov, V. A. Shlyapochnikov, V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.* **1995**, 2187−2189 (*Russ. Chem. Bull.* **1995**, *44*, 2093−2095). [8b] K. I. Rezchikova, A. M. Churakov, V. A. Shlyapochnikov, V. A. Tartakovsky, *Mendeleev Commun.* **1995**, 100−102. [8c] K. I. Rezchikova, A. M. Churakov, K. Ya. Burshtein, V. A. Shlyapochnikov, V. A. Tartakovsky, *Mendeleev Commun.* **1997**, 174−175.

[9] A. M. Churakov, O. Yu. Smirnov, S. L. Ioffe, Yu. A. Strelenko, V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.* **1994**, 1620−1623 (*Russ. Chem. Bull.* **1994**, *43*, 1532−1535).

[10] D. L. Lipilin, A. M. Churakov, Yu. A. Strelenko, V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.,* **2002**, 291−301.

[11] R. C. Zawalski, P. Kovacic, *J. Org. Chem.* **1979**, *44*, 2130−2133.

[12] A. E. Frumkin, A. M. Churakov, Yu. A. Strelenko, V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.* **2000**, 480−484 (*Russ. Chem. Bull.* **2000**, *49*, 482−486).

[13] The ring nitration of BTDOs proceeded when HNO_3/H_2SO_4 nitrating mixture was used. See our further publications in: *Izv. Akad. Nauk, Ser. Khim (Bull. Acad. Sci. USSR, Div. Chem. Sci.*).

[14] W. M. Weaver, in: *The Chemistry of the Nitro and Nitroso Groups* (Ed.: H. Feuer), Interscience Publishers, New York, **1970**, part 2, pp. 35−37.

[15] A. M. Churakov, S. E. Semenov, S. L. Ioffe, Yu. A. Strelenko, V. A. Tartakovsky, *Izv. Akad. Nauk, Ser. Khim.* **1997**, 1081−1082 (*Russ. Chem. Bull.* **1997**, *46*, 1042−1043).

[16] The NMR study of this reaction will be published elsewhere.

[17] R. W. Darbeau, E. H. White, F. Song, N. R. Darbeau, J. Chou, *J. Org. Chem.* **1999**, *64*, 5966−5978, and references cited therein.

[18] [18a] A. Mitschker, K. Wedemeyer, *Synthesis* **1988**, 517−520. [18b] A. J. Boulton, M. Kiss, J. D. K. Saka, *J. Chem. Soc., Perkin Trans. 1* **1988**, 1509−1512.

[19] A. M. Churakov, S. L. Ioffe, Yu. A. Strelenko, V. A. Tartakovsky, *Tetrahedron Lett.* **1996**, *37*, 8577−8580.

[20] O. A. Luk'yanov, V. P. Gorelik, V. A. Tartakovsky, S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 1804−1805 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1971**, *20*, 1696−1697).

[21] W. D. Emmons, A. S. Pagano, T. E. Stevens, *J. Org. Chem.* **1958**, *23*, 311−313.

[22] R. G. Gafurov, B. S. Fedorov, L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 383−386 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1977**, *26*, 345−348).

[23] [23a] A. M. Churakov, O. Yu. Smirnov, Yu. A. Strelenko, S. L. Ioffe, V. A. Tartakovsky, Yu. T. Struchkov, F. M. Dolgushin, A. I. Yanovsky, *Mendeleev Commun.* **1994**, 122−123. [23b] D. L. Lipilin, O. Yu. Smirnov, A. M. Churakov, Yu. A. Strelenko, S. L. Ioffe, V. A. Tartakovsky, *Eur. J. Org. Chem.*, submitted.

[24] In ^{14}N NMR spectra of polyazines, the signals of the *N*-oxide nitrogen atoms are the narrowest: L. Stefaniak, *Spectrochim. Acta* **1976**, *32a*, 345−349.

[25] [25a] G. J. Martin, M. L. Martin, J.-P. Goeusnard, ^{15}N NMR spectroscopy, Springer-Verlag, Berlin, **1981**, p. 168. [25b] Ref.[25a], p. 166.

[26] A similar reaction involves the replacement of the *tert*-butylazoxy group by the nitro group in electrophilic nitration of substituted *para*-(*tert*-butylazoxy)anilines: A. E. Frumkin, A. M. Churakov, Yu. A. Strelenko, V. V. Kachala, V. A. Tartakovsky, *Org. Lett.* **1999**, *1*, 721−724.

[27] For 2-nitro-1-phenyldiazene 1-oxide Ph−N(O)=N−NO$_2$, ^{15}N NMR (30.42 MHz, δ from CH_3NO_2, $CDCl_3$) δ = −45.5 ppm (N→O), −34.0 (−N=), −5.9 (NO$_2$). For synthesis of this compound, see: A. M. Churakov, S. L. Ioffe, V. A. Tartakovsky, *Mendeleev Commun.* **1996**, 20−22.

[28] A. M. Churakov, V. A. Tartakovsky, *Energetic Materials. Production, Processing and Characterization, 29th International Annual Conference of ICT, Karlsruhe, Germany*, DWS Werbeagentur und Verlag GmbH, Karlsruhe, Germany, **1998**, V7.

[29] G. A. Olah, S. J. Kuhn, *Org. Synth.* **1967**, *47*, 56.

[30] G. V. Caesar, M. Goldfrank, *J. Am. Chem. Soc.* **1946**, *68*, 372−375.

[31] J. H. Robson, *J. Am. Chem. Soc.* **1955**, *77*, 107−108.

[32] J. J. Ritter, P. P. Minieri, *J. Am. Chem. Soc.* **1948**, *70*, 4045−4048.

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