A New Cyclization Involving the Diazonium and *ortho*-(*tert*-Butyl)-*NNO*-azoxy Groups − Synthesis of 1,2,3,4-Benzotetrazine 1-Oxides

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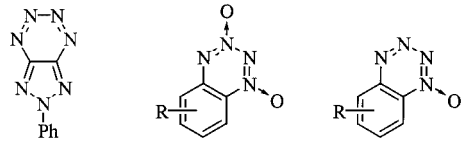
The synthesis of 1,2,3,4-benzotetrazine 1-oxides (BTOs) is described. Bromo-BTOs **4b**–**d** were prepared by the intramolecular cyclization of diazonium salts bearing an *ortho*-(*tert*-butyl)-*NNO*-azoxy group. BTOs bearing electron-releasing substituents were obtained by nucleophilic displacements of bromine in **4b**–**d**. The formation of the BTO cyclic system involves the intermediate 2-(*tert*-butyl)-1,2,3,4-benzotetrazinium 4-oxides, which arise from an *N*,*N*-[1,2]-shift of the *tert*-butyl group. Decomposition of BTOs involves opening of the tetrazine ring to afford *ortho*-azidonitroso derivatives, followed by their cyclization with the evolution of the N_2 molecule to give benzofurazans.

Introduction

1,2,3,4-Tetrazines are among the basic six-membered azaaromatics,[1] but they are nevertheless poorly investigated. The only unambiguous 1,2,3,4-tetrazine, 2-phenyl-2*H*-[1,2,3]triazolo[4,5-*e*][1,2,3,4]tetrazine (PTT), was synthesized by A. Ohsawa et al., by oxidation of annulated 1-amino-1,2,3-triazole.[2] However, this approach failed in the benzene series. For example, the oxidation of 1-*N*-aminobenzotriazole did not yield 1,2,3,4-benzotetrazine,[3] although this species was considered among the possible unstable intermediates in this reaction. Be that as it may, 1,2,3,4-tetrazines are believed to be not particularly stable. PTT slowly decomposes at room temperature through stepwise N_2 elimination.[2]



PTT BTDO BTO

We have recently described the synthesis of 1,2,3,4-benzotetrazine 1,3-dioxides (BTDOs) and demonstrated that the presence of two *N*-oxide atoms located in the 1- and 3-positions considerably improves the thermal stability of 1,2,3,4-tetrazine rings.[4] The question of the stability of mono *N*-oxides of 1,2,3,4-benzotetrazines (BTOs) was an open one until recently. In preliminary communications we have described the synthesis and X-ray study of the first representative of the 1,2,3,4-tetrazine 1-oxides, 5,7-dibromo-1,2,3,4-benzotetrazine 1-oxide,[5] and the plausible mechanism of its formation.[6] Here we describe detailed results on the synthesis and stability of BTOs.

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Results and Discussion

A synthetic pathway to BTOs **4** involves the intramolecular cyclization of the diazonium tetrafluoroborates **2** to afford cyclic salts **3**, followed by elimination of the *tert*-butyl cation (Table 1, reactions A−C). BTOs **4** in turn undergo opening of the tetrazine ring to give *ortho*-azidonitrosobenzenes **5**, followed by cyclization to benzofurazans **6** (reactions D, E, Table 1).

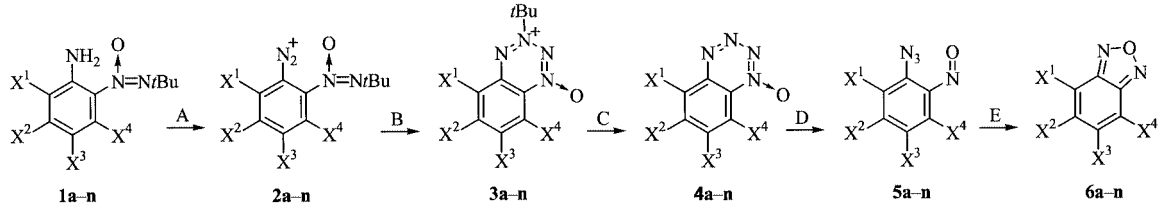
The relative rates of each stage of the transformations **1** → **6** and the stabilities of the respective intermediates **2**−**5** depend on the substituents on the benzene ring.

Diazonium Salts 2

Diazonium tetrafluoroborates **2** were prepared by treatment of anilines **1** with $NOBF_4$ at −15 → 0 °C in MeCN solution (Table 1, reaction A). The preparations of the starting anilines **1**, except for those of anilines **1l** and **1n**, were described previously.[7−9] Anilines **1l** and **1n** were synthesized by bromination of the appropriate anilines, as shown in Scheme 1.

The structures of salts **2** were confirmed by spectral studies. The salt **2a** was investigated most thoroughly,[5] as it was stable in solution at room temperature . The ^{1}H NMR spectrum of this salt has the signal of the *tert*-butyl group at δ = 1.53 ppm, the ^{13}C NMR shows the expected shifts of the benzene ring,[10] and the ^{14}N NMR spectrum exhibits

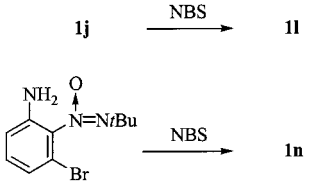
Table 1. The reaction conditions used for and the yields of compounds **2a**−**n** to **6a**−**n** in the series of transformations **1** → **2** → **3** → **4** → **5** → **6**



1a–n **2a–n** **3a–n** **4a–n** **5a–n** **6a–n**

	X^1	X^2	X^3	X^4	**2**[a]	**3**[a]	**4**[a]	**5**[a]	**6**[a]
a	H	H	H	H	94 %	50 °C, 1 h, (50 %)[b][c]	[d]	[d]	reflux, 1 h, or room temp., 8 h, 84 %[b] − room temp., 1 h, (95 %)[e]
b	Br	H	Br	H	95 %	room temp., 10 min, 69 %[b] − without solvent, 40 °C, 12 h, 56 %[b]	5 °C, 2 days, 60 %[e] − 40 %[b] − SiO_2, 40 °C, 15 min, 55 %[b]	0 °C, 2 h, 40 %[f]	room temp., 1 day 95 %[f]
c	Br	Br	Br	H	[d]	85 %[g]	room temp., 1 h, 20 %[e]	0 °C, 30 min, (30 %)[c,f]	room temp., 2 h, 92 %[e]
d	Br	H	Me	Me	60 %	0 °C, 10 min (10 %)[b,c]	room temp., 2 h, 50 %[b]	[d]	room temp., 2 days, 80 %[b]
e	Br	Me	Br	H	85 %	5 °C, 4 h, 62 %[b]	0 °C, 2 days, 10 %[e]	0 °C, 2 days, (8 %)[c,b]	room temp., 1 day, 85 %[f]
f	H	H	Br	H	89 %	room temp., 10 min, 43 %[b] − without solvent, 40 °C, 4 days, 69 %[b]	0 °C, 2.5 h, (15 %)[c,e]	[d]	0 °C, 20 h, 90 %[b] − room temp., 20 min, 90 %[f]
g	H	Br	Br	H	88 %	0 °C, 5 h, (30 %)[b]	room temp., 30 min, (40 %)[b]	[d]	room temp., 2 h, 83 %[b]
h	Br	H	Me	H	95 %	0 °C, 2 h, 85 %[b]	[d]	[d]	room temp., 20 h, 75 %[b]
i	H	Br	H	H	90 %	5 °C, 3 h, (15 %)[b]	[d]	[d]	room temp., 2 h, 80 %[b]
j	H	H	NO_2	H	[h]	[h]	[h]	[h]	0 °C, 10 min, 60 %[g]
k	NO_2	H	H	H	[h]	[h]	[h]	[h]	0 °C, 20 min, 70 %[g]
l	Br	H	NO_2	H	[h]	[h]	[h]	[h]	−5 °C, 10 min, 82 %[g]
m	H	Br	H	Br	[h]	[h]	[h]	[h]	5 °C, 10 min, 65 %[g]
n	Br	H	Br	Br	[h]	[h]	[h]	[h]	0 °C, 30 min, 80 %[g]

[a] MeCN as solvent (or CD_3CN in ^1H NMR experiments); the isolated yields; in parentheses the best yields observed by in situ ^1H NMR monitoring. [b] Starting from diazonium salt **2**. [c] [D_6]acetone as a solvent. [d] Not observed in situ by ^1H NMR. [e] Starting from cyclic salt **3**. [f] Starting from BTO **4**. [g] Starting from aniline **1**. [h] Not observed by TLC.



Scheme 1

the expected signals for the positively charged nitrogens of the azoxy group[11] (δ = −66 ppm) and the diazonium group[10] (−*N*≡N^+, δ = −154 ppm). The ^{15}N NMR/INEPT spectrum shows a signal for the nitrogen connected with the *tert*-butyl group[11] (δ = −7 ppm). IR spectroscopy also confirmed the presence of the diazonium group (KBr, $\tilde{\nu}$ = 2300 cm^{-1}). The salt **2a** therefore unambiguously has the structure of the open-chain diazonium salt. The diazonium salts **2b** and **2d**−**i** show similar spectroscopic characteristics (see Exp. Sect.).

Certain salts bearing electron-withdrawing substituents are so highly reactive that it is impossible to isolate them (Table 1). This is true for diazonium salts with three bromine atoms (**2c**) or with nitro groups (**2j**−**l**), and also for salts **2m** and **2n**, in which X^4 = Br.

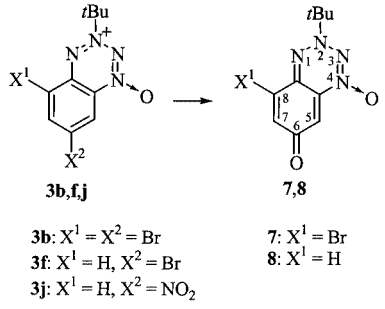
Cyclic Salts 3

The transformations of the diazonium salts **2** into the cyclic salts **3** involve cyclization followed by the [1,2]-shift of the *tert*-butyl group (Table 1, reaction B). The feasibility of the isolation of cyclic salts **3** depends on the relative rates of their generation and of further elimination of the *tert*-butyl group.

The structures of salts **3** were confirmed by spectral studies and chemical reactions, salt **3b** being investigated most thoroughly.[5] In the IR spectrum of this salt, the absorption band of the diazonium group has disappeared, as has the ^{14}N signal of this group. The downfield shift of the *tert*-butyl group in the ^1H NMR spectrum (δ = 2.08 ppm) and

the downfield shift of the tertiary carbon atom of this group in the ^{13}C NMR spectrum (δ = 85.8 ppm) indicate that the *tert*-butyl group is linked with a strong electronegative moiety. All these data suggested the cyclic structure.

Further evidence for the **3b** structure was gained on treatment of **3b** with water. The hydrolysis of **3b** in DMSO solution containing H_2O (or in MeCN/20 % DMSO/1 % H_2O solution) proceeds in few minutes at room temperature and results in replacement of the bromine atom to give the quinoid cycle **7** (40 %) (Scheme 2). Treatment of the solution of **3b** in MeCN/H_2O with a small amount of a base (e.g., $NaHCO_3$) also results in the rapid formation of **7**, but the yield is worse than in the previous case. The structure of **7b** was established by an X-ray diffraction study.[6] From this structure we were able to verify the structure of salt **3b**, and so we conclude that diazonium salt **2b** turns into cyclic salt **3b** through the *N*,*N*-[1,2]-migration of the *tert*-butyl group. The possible mechanism of this rearrangement is discussed below.



Scheme 2

The reactions between water and salts **3** bearing leaving groups in the 6-position are common in character. Thus, the salt **3f** (X^2 = Br)[6] gave rise to quinoid compound **8**. Further work on the reactions of salts **3** with nucleophiles is in progress.

Diazonium salt **2a** did not cyclize into **3a** in the absence of solvent (only tarry products were observed). In solutions the cyclization proceeded rather slowly (Table 1). The transformations of **2a** were monitored in situ by ^1H NMR spectroscopy. Heating of this salt in CD_3CN solution at 50 °C for 1 h furnished a mixture of unchanged **2a**, intermediate **3a**, and benzofurazan **6a** (in the 4:5:1 ratio). Further heating caused a decrease in the concentration of **3a** while **2a** remained present in the reaction mixture, and so we failed to isolate **3a** in a pure state.

The cyclizations of **2b**, **2e**, **2f**, and **2h** were complete within a few minutes at room temperature in solution, affording the cyclic salts **3b**, **3e**, **3f**, and **3h** in good yields. The salts **3b** and **3f** were also obtained in good yield when diazonium salts **2b** and **2f** were allowed to stand without solvent at 40 °C (Table 1).

The cyclization of diazonium salt **2c** in MeCN solution was very fast (the salt was not observed in situ by ^1H NMR). The elimination of the *tert*-butyl group from the resulting salt **3c** was much slower, and **3c** was isolated in good yield (85 %).

Diazonium salt **2d**, **2g**, and **2i** cyclized readily at 0 °C, but further transformation of **3d**, **3g**, and **3i** into BTOs proceeded too easily, and these salts were not isolated in pure states. Nevertheless, they were observed by ^1H NMR.

Diazonium salt **2j**, with a nitro group in the *para*-position, was very reactive. It was impossible to isolate the cyclic salt **3j**, however, because further reactions resulting in furazan **6j** proceed very rapidly (Table 1). At the same time, treatment of the MeCN solution of **2j** with DMSO/H_2O at −20 °C gave the quinoid compound **8** in 40 % yield (Scheme 2), indicating that the real intermediate was the cyclic salt **3j**. Other diazonium salts bearing the nitro group (**2k**, **2l**) and salts bearing bromine in the position *ortho* to the *tert*-butylazoxy group (**2m**, **2n**) behave similarly to **2j** (Table 1).

BTOs 4

The possibility of the isolation of BTOs **4** depends on the relative rates of their generation and of further ring-opening. We failed to synthesize the parent BTO **4a**. The cyclic salt **3a** (as a mixture with diazonium salt **2a** and furazan **6a**) decomposed completely within 1 h at room temperature, and **4a** was not observed (^1H NMR monitoring). This was also the case for BTO **4i**.

The conversion of **3b** proceeded smoothly when this salt was dissolved in MeCN in the presence of a small amount of H_2O. Substitution of bromine atom, resulting in **7**, did not take place. Instead, slow elimination of the *tert*-butyl group occurred, to afford BTO **4b** (60 % yield after two days at 5 °C, Table 1), *N*-(*tert*-butyl)acetamide (45 % yield, based on ^1H NMR), and *t*BuOH (55 % yield, based on ^1H NMR). *N*-(*tert*-Butyl)acetamide could have formed as a result of capture of the *tert*-butyl cation by MeCN, followed by hydrolysis of the intermediate salt. The formation of BTO slowed down when dry MeCN was used as solvent, and the yield of BTO fell, owing to its decomposition into furazan. In wet MeCN it was possible to obtain **4b** directly from the diazonium salt **2b** in 40 % yield. It was found that the elimination of the *tert*-butyl group from **3b** was markedly accelerated on silica gel. BTO **4b** was obtained in 55 % yield when the powdered salts **2b** or **3b** were placed on a silica gel pad and eluted with warm $CHCl_3$ (40 °C) for 15 min; this is the most convenient procedure for the synthesis of **4b**. However, we failed to extend this procedure to other salts. The structure of BTO **4b** was confirmed by X-ray investigations.[6]

The BTOs **4c−e** were isolated in the same way. BTOs **4f** and **4g** were obtained in solution as mixtures with the corresponding furazans.

The cyclic salt **3h** is reasonably stable. The decomposition of this salt is too slow (Table 1), and it was impossible to observe BTO **4h** by ^1H NMR.

Elimination of the *tert*-butyl group from the cyclic salts **3j−n** proceeded very quickly (a few min at 0 °C) but it was impossible to isolate BTOs **3j−n**, owing to their instability.

ortho-Azidonitrosobenzenes 5

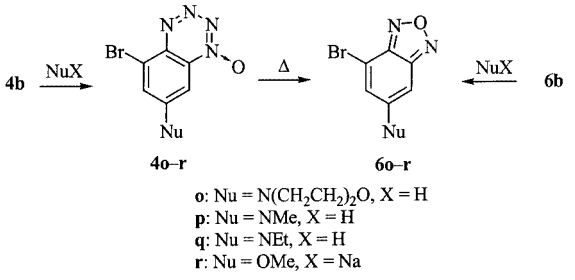
Of the *ortho*-azidonitrosobenzenes **5** investigated, the most stable was **5b**. To the best of our knowledge, **5b** is the first isolated *ortho*-azidonitrosobenzene.[12] It was obtained as a yellow solid in no less than 95 % purity. The characteristic features of **5b** are the upfield shifts of the C-2 (δ = 110 ppm) and 2-H (δ = 6.23 ppm) signals, and the typical IR spectrum ($\tilde{\nu}$ = 2120, 2150 cm^{-1}, N_3) and ^{14}N NMR spectrum ($-N{=}N{=}N$, δ = −143 ppm).[5] According to ^1H NMR and ^{13}C NMR, **5b** exists as a monomer in solutions. Its solutions are yellow in color rather than green, which is probably due to the strong conjugation between the azido and nitroso groups.

Azidonitrosobenzene **5b** slowly eliminates N_2 at room temperature to give benzofurazan **6b** (Table 1, reaction E). The other azidonitrosobenzenes investigated proved to be less stable. Only **5c** and **5e** were observed in situ by ^1H NMR.

Nucleophilic Displacement in BTOs

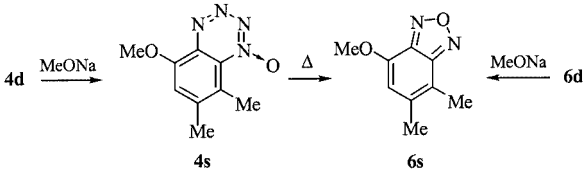
From the above discussion it follows that BTOs with electron-releasing substituents are impossible to obtain by cyclization of diazonium salts, owing to the low reactivity of these salts **2** and the relatively high stability of the corresponding salts **3**. However, such BTOs can be synthesized from BTOs **4b−d** by nucleophilic displacement.

Treatment of BTO **4b** with nucleophiles (secondary amine/MeCN or MeONa/MeOH) results in replacement of the bromine in the 7-position to yield BTOs **4o−r** (Scheme 3).



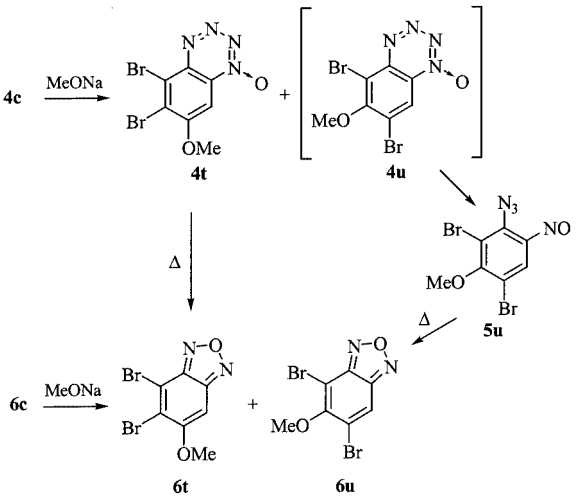
Scheme 3

BTO **4d** reacts with sodium methoxide to afford BTO **4s** (Scheme 4).



Scheme 4

In the case of **4c**, competitive substitution in the 6- and the 7-positions took place (Scheme 5). However, only BTO **4t** was isolated, because BTO **4u**, with a methoxy group in the 6-position, proved to be unstable and readily gave *ortho*-azidonitrosobenzene **5u**.

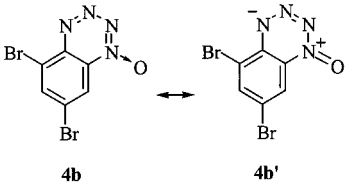


Scheme 5

On heating, BTOs **4o−t** and azidonitrosobenzene **5u** were transformed into the corresponding furazans. To confirm their structures, these compounds were also obtained from bromofurazans **6b−d** by nucleophilic displacement.

Stability of BTOs

As shown by X-ray studies, the cyclic conjugation in the tetrazine moiety of **4b** is much more pronounced than in triazolotetrazine PTT, as follows from the uniformity of the N(1)−N(2) and N(2)−N(3) bond lengths in **4b** (1.34 Å and 1.35 Å, respectively).[6] The relevant bond lengths in PTT are noticeably different from one another (1.31 Å and 1.39 Å, respectively).[2] This distinction may be due to the electron-releasing effect of the *N*-oxide oxygen atom, as reflected in the considerable contribution of the **4b′** resonance form. In this respect BTOs resemble benzo-1,2,3,4-terazine 1,3-dioxides, in which strong cyclic conjugation is also observed.[13]

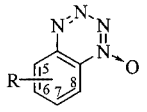


However, the conjugation in the tetrazine ring does not markedly stabilize the **4b** molecule. The irreversible opening of the ring takes place slowly at room temperature, to afford the open-chain tautomer *ortho*-azidonitrosobenzene **5b** (Table 1, reaction D). It should be noted that this decomposition pathway of the annulated tetrazine 1-oxide ring differs distinctly from that of annulated 1,2,3,4-tetrazines[2] and 1,2,3,4-tetrazine 1,3-dioxides.[4]

We can draw preliminary conclusions about the relative thermal stabilities of BTOs. The times required for com-

plete decomposition of BTOs **4b−g** and **4o−t** in MeCN solution are presented in Table 2.

Table 2. The times required for complete decomposition of BTOs **4b−g** and **4o-t** in MeCN solution (initial concentration $15 \cdot 10^{-3}$ mol/L)



4

BTO **4**	Substituents R	*T* [°C]	Time
4b	5,7-Br_2	20	1 day
4c	5,6,7-Br_3	20	1 h
4d	5-Br-7,8-Me_2	50	8 h
		20	8 days
4e	5,7-Br_2-6-Me	20	1 day
4f[a]	7-Br	20	20 min
4g[a]	6,7-Br_2	20	30 min
4o	5-Br-7-morph	50	12 h
4p	5-Br-7-Me_2N	50	9 h
4q	5-Br-7-Et_2N	50	9 h
4r	5-Br-7-MeO	20	7 h
4s	5-MeO-7,8-Me_2	20	1 h
4t	5,6-Br_2-7-MeO	20	1 h

[a] The BTO is inaccessible in a pure state and is obtained in acetonitrile solution.

In a number of cases, BTOs are unstable under the reaction conditions used (Table 1) and unobservable by NMR spectroscopy, but we can nevertheless infer conclusions about their stabilities relative to other BTOs. At 20 °C in CD_3CN solution, the cyclic salt **3a** (15 mmol/L, as a mixture with furazan, ^1H NMR monitoring) decomposed completely in 1 h, and **4a** was not detected. Compound **4a** must therefore be less stable than **4b** (R = 5,7-Br_2), which decomposed completely in 1 day (Table 2). Diazonium salt **2j** decomposed completely to furazan in a few min at 0 °C (Table 1), so BTO **4j** (R = 7-NO_2) is accordingly less stable than **4f** (R = 7-Br). Similar conclusions can be drawn about BTOs **4k−n**.

The electron-releasing methyl group might stabilize the molecule of **4h** in relation to **4b**. However, we cannot compare BTO **4h** with **4b**, as the cyclic salt **3h** is too stable and decomposed only in 20 h at 20 °C. We can only say that **4h** is less stable than BTO **4d**, which decomposes in 8 days at room temperature.

Allowing for these considerations, as well as the data from Table 2, the BTDOs were arranged in order of decreasing stability: **4o** > **4d/4p/4q** > **4b/4e** > **4r** > **4c/4s/4t** > **4f/4g** > **4j−n**. The storage life of BTOs in the solid state without distinct decomposition is a week at 20 °C for **4d** and **4o−q**, 2−3 days at 20 °C for **4b**, **4e**, and **4r**, and 2−3 days at −5 °C for **4c**, **4s**, and **4t**. It should be noted that although **4b** is more stable than **4r** in solution, the latter compound becomes more stable in the solid state.

The factors that increase the stability of BTOs are as follows: bromine atoms in the 5- and 7-positions, a methyl group in the 8-position, and the replacement of a bromine atom in the 7-position with a strongly electron-releasing group (NR_2). The factors that decrease the stability of BTOs include: the replacement of a hydrogen in the 6-position of BTO **4b** by a bromine atom, the replacement of a bromine atom in the 5-, 6-, or 7-positions by the methoxy group, and the replacement of a bromine atom in the 7-position by a nitro group.

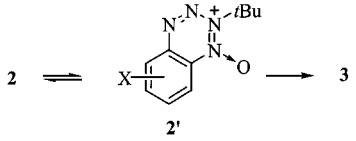
As mentioned above, the first stage of decomposition of BTOs is the irreversible opening of the tetrazine cycle to give azidonitrosobenzenes. It is this reaction that determines the stability of BTOs. To discuss the influence of substituents, however, it is more reasonable to consider the reverse reaction: the interaction of the azido and nitroso groups, in which the terminal nitrogen of the azido group plays the role of a nucleophile and the nitroso group the role of an electrophile. In this reaction, electron-releasing substituents (e.g., Me_2N) in the position *para* to the azido group should increase the negative charge on this group and accelerate ring-formation. Electron-withdrawing substituents (e.g., NO_2) would act in the opposite way. At the same time, electron-releasing substituents (e.g., MeO) *para* to the nitroso group should increase the negative charge on this group and slow down the ring formation. Thus, strong electron donors in the 7-position should stabilize the tetrazine cycle, while electron donors in the 6-position and electron acceptors in the 7-position should destabilize it.

This simple reasoning explains the increases in stability for most BTOs. However, it fails to explain why replacement of the 7-bromine atom in **4b** by the methoxy group does not stabilize the molecule in solution.

Steric factors are also of great importance. The decreases in stability due to the bromine atoms in the 6-position of BTO **4c** or in the 8-position of BTO **4n** are probably for this reason. However, it is still unclear why the methyl group in the 8-position increases the stability of **4d**. The increase in stability due to bromine in the 5-position (BTO **4b**) is also not quite clear. Additional information is required to explain these facts.

Mechanism of the N,N-Migration

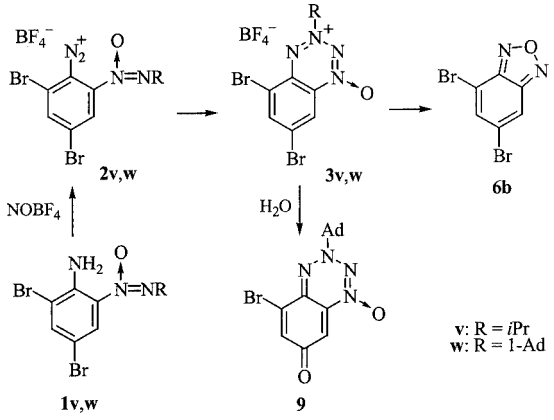
The mechanism of the rearrangement of diazonium salts **2** to cyclic salts **3** (Table 1, reaction B) deserves further consideration. The first stage of this reaction is believed to be the reversible formation of the cycle **2′** (Scheme 6), while the second stage would be the irreversible migration of the *tert*-butyl group. The driving force of the migration might be the higher thermodynamic stability of salt **3** than of **2′**. Semiempirical calculations (PM-3 method) show that salts **3** are 7−8 kcal/mol more favorable than salts **2′**. This type of *N,N*-[1,2]-migration of alkyl groups in cationic systems has not been described previously.[14] The intermediates **2′** were found to be a short-lived species, and we never observed them during in situ ^1H NMR monitoring of the reaction.



Scheme 6

A priori, the migration of the *tert*-butyl group can be accommodated by an elimination−addition mechanism involving a tight ionic pair, or by a simultaneous mechanism with a three-center, two-electron transition state. The argument in support of the latter mechanism is the fact that the rearrangement takes place not only in solution, but also in the solid state (**3b**, **3f**, Table 1), whereas the former mechanism would need solvation.

To obtain additional information about the rearrangement, diazonium salts **2v** and **2w**, with isopropyl and 1-adamantyl substituents, respectively, at the azoxy groups, were synthesized (Scheme 7).



Scheme 7

Reaction of the isopropyl derivative **2v** began only when this salt was heated to 130 °C without solvent. The ^{1}H NMR analysis of the residue showed 85 % of the unchanged **2v** after 30 min heating. Furazan **6b** was not observed at all. The adamantyl derivative **2w** proved to be more reactive than its isopropyl counterpart, but much less reactive than the *tert*-butyl derivative **2b**. Its ^{1}H NMR in CD_3CN showed 85 % of unchanged **2w** and 15 % of the furazan **6b** after 10 days at room temperature. The yield of furazan **6b** increased to 60 % after 5 h at reflux in MeCN. The cyclic salt **3w** was not observed in these experiments. However, when the diazonium salt **2w** was treated with DMSO/H_2O at room temperature, a 23 % yield of quinoid cycle **9** was obtained in 10 min, indicating that migration of the adamantyl group took place under these conditions and **3w** was the real intermediate. Such a strong dependence of the reaction rate upon the solvent counts in favor of the elimination−addition mechanism of the rearrangement in the case of the adamantyl group. It should be noted that DMSO did not accelerate the reaction so much in the case of the *tert*-butyl derivatives. The rate of formation of furazan **6a** from diazonium salt **2a** in MeCN, for example, is practically the same as in DMSO solution.

Conclusion

In conclusion, the synthetic route to BTOs involves cyclization of diazonium salts **2**, bearing *ortho*-(*tert*-butyl)azoxy groups, to give the salts **3**. Subsequent elimination of the *tert*-butyl cation affords BTOs. This method can be used for the synthesis of BTOs with a limited set of substituents (e.g., 5,7-Br_2-BTO). BTOs bearing strongly electron-releasing groups (e.g., R_2N) cannot be obtained in this way. The reason for this is that these groups increase the stability of the diazonium salts **2** and the cyclic cationic salts **3**, which means that both the cyclization reaction and the elimination of the *tert*-butyl group take place at excessively high temperatures. Nevertheless some BTOs with strongly electron-releasing groups can be synthesized by nucleophilic displacement.

A plausible mechanism for the formation of cyclic tetrazinium salts **3** involves the intramolecular nucleophilic attack of the diazonium ion at the distal *N*-atom of the *tert*-butylazoxy group, followed by the *N*,*N*-[1,2]-shift of the *tert*-butyl group. In some cases salts **3** can be isolated in good yields.

The stability of BTOs depends upon the substituents on the benzene ring. Some BTOs (e.g., 7-R_2N-BTOs) are stable at room temperature for several days, whereas others are unstable even at 0 °C (e.g., 7-NO_2-BTOs). The decomposition of BTOs involves opening of the tetrazine ring to afford *ortho*-azidonitrosobenzenes followed by evolution of the N_2 molecule and formation of furazans.

Experimental Section

General Remarks: NMR spectra were recorded with a Bruker AM 300 instrument (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 21.69 MHz for ^{14}N and 30.42 MHz for ^{15}N); chemical shifts are δ units downfield from internal TMS (^{1}H, ^{13}C) or external CH_3NO_2 (^{14}N, ^{15}N). Negative values of δ_N correspond to upfield shifts. In some cases the assignment of the ^{13}C NMR signals were made by calculations, using additive schemes. Mass spectroscopic data were obtained at 70 eV by electron impact. Melting points were determined with a Kofler apparatus and are uncorrected. Anilines **1a**, **1c−e**, **1g−i**, **1v**, and **1w**,[8] **1b**, **1f**, and **1m**,[7] **1j** and **1k**,[9] and 3-bromo-2-(*tert*-butyl-*NNO*-azoxy)aniline[15] were prepared as described previously.

2-Bromo-6-(*tert*-butyl-*NNO*-azoxy)-4-nitroaniline (1l): NBS (80 mg, 0.46 mmol) was added to a solution of aniline **1j** (100 mg, 0.46 mmol) in CH_2Cl_2 (15 mL). After the mixture had been stirred for 5 h at room temperature, the solvent was evaporated in vacuo and the residue was purified by chromatography (silica gel, $CHCl_3$) to yield 125 mg (86 %) of **1l**, m.p. 115−117 °C. ^{1}H NMR ([D_6]DMSO): δ = 1.47 (s, 9 H, *t*Bu), 7.7 (br. s, 2 H, NH_2), 8.42 (d, *J* = 1.8 Hz, 1 H, 3-H), 8.71 (d, *J* = 1.8 Hz, 1 H, 5-H) ppm. ^{14}N NMR ([D_6]DMSO): δ = −17 ($\Delta\nu_{1/2}$ = 170 Hz, NO_2), −54 ($\Delta\nu_{1/2}$ = 290 Hz, N→O) ppm. IR (KBr): $\tilde{\nu}$ = 1460 cm^{-1} [N(O)=N],

1540, 1360 (NO_2), 3340, 3440 (NH_2). MS (70 eV): *m*/*z* (relative intensities) = 316, 318 (1:1) [M^+]. $C_{10}H_{13}BrN_4O_3$ (317.14): calcd. C 37.87, H 4.13, Br 25.20, N 17.67; found C 37.92, H 4.12, Br 25.14, N 17.83.

3,4,6-Tribromo-2-(*tert*-butyl-*NNO*-azoxy)aniline (1n): NBS (200 mg, 1.1 mmol) was added to a solution of 3-bromo-2-(*tert*-butyl-*NNO*-azoxy)aniline (150 mg, 0.55 mmol) in CH_2Cl_2 (10 mL). After 3 h stirring at room temperature, the reaction mixture was worked up as in the previous case to yield 190 mg (80 %) of **1n**, m.p. 131−132 °C. ^{1}H NMR ([D$_6$]acetone): δ = 1.5 (s, 9 H, *t*Bu), 5.2 (br. s, 2 H, NH_2), 8.87 (s, 1 H, 5-H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 25.8 (C*Me*$_3$), 61.2 (*C*Me$_3$), 110.2, 112.0, 118.7, 134.1, 136.3 (C-5) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −54 ($\Delta\nu_{1/2}$ = 80 Hz, N→O) ppm. IR (KBr): $\tilde{\nu}$ = 1450 cm^{-1} [N(O)=N], 3330, 3450 (NH_2). MS (70 eV): *m*/*z* (relative intensities) = 426, 428, 430, 432, 434 (1:3:5:3:1) [M^+]. $C_{10}H_{12}Br_3N_3O$ (429.93): calcd. C 27.94, H 2.81, Br 55.76, N 9.77; found C 37.99, H 2.81, Br 55.32, N 9.81.

General Procedure for the Diazotization of Anilines 1: A solution of aniline **1** (1.42 mmol) in dry MeCN (5 mL) was added dropwise at −15 °C over a period of 10 min to a stirred suspension of $NOBF_4$ (200 mg, 1.71 mmol) in dry MeCN (15 mL). After an additional 15 min stirring at −15 °C, the solution was concentrated ca. 90 % in vacuo at a temperature of 0 °C. Cooled Et_2O was added to the resultant suspension. The precipitate was filtered off and washed with cooled Et_2O and then with pentane and dried in vacuo in an ice-cooled bath.

2-(*tert*-Butyl-*NNO*-azoxy)phenyldiazonium Tetrafluoroborate (2a): Colorless solid (390 mg, 94 %), m.p. 141−145 °C (decomp.). ^{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. ^{1}H NMR (CD_3CN): δ = 1.53 (s), 8.12 (dt, 5-H), 8.39 (dt, 4-H), 8.59 (dd, 3-H), 8.73 (dd, 6-H) ppm. ^{13}C NMR[16a−16e] ([D$_6$]acetone): δ = 25.4 (CH_3), 61.9 (*C*Me$_3$), 110.9 (C-1, ^3J = 9.2, ^2J = 3.8 Hz), 127.1 (C-3, ^3J = 14.0, ^3J = 8.2 Hz), 134.8 (C-5, ^3J = 8.2 Hz), 137.1 (C-6, ^3J = 8.7, ^2J = 3.2 Hz), 143.1 (C-4, ^3J = 8.2 Hz), 146.7 (br., C-2) ppm. ^{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): $\tilde{\nu}$ = 1500 cm^{-1} [N(O)=N], 2300 (N_2^+). $C_{10}H_{13}BF_4N_4O$ (292.04): calcd. C 41.13, H 4.49, N 19.18; found C 41.21, H 4.53, N 18.79.

4,6-Dibromo-2-(*tert*-butyl-*NNO*-azoxy)phenyldiazonium Tetrafluoroborate (2b): Yellow solid (610 mg, 95 %), m.p. 125−129 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 1.52 (s, 9 H, *t*Bu), 8.93 (d, *J* = 1.8 Hz, 1 H, 3-H), 8.98 (d, 1 H, 5-H) ppm. ^{13}C NMR[16b] (273 K, ([D$_6$]acetone): δ = 25.1 (CH_3), 62.8 (*C*Me$_3$), 130.0 (C-3), 141.7 (C-5) ppm. The rest of the signals were unrecordable, due to the low solubility of the salt. ^{14}N NMR ([D$_6$]acetone): δ = −69 ($\Delta\nu_{1/2}$ = 100 Hz, N→O), −153 ($\Delta\nu_{1/2}$ = 250 Hz, -*N*$^+$≡N) ppm. IR (KBr): $\tilde{\nu}$ = 1490 cm^{-1} [N(O)=N], 2270 (N_2^+). $C_{10}H_{11}BBr_2F_4N_4O$ (449.83): calcd. C 26.70, H 2.46, N 12.46; found C 26.53, H 2.52, N 12.63.

6-Bromo-2-(*tert*-butyl-*NNO*-azoxy)-3,4-dimethylphenyldiazonium Tetrafluoroborate (2d): Yellow solid (340 mg, 60 %), m.p. 120−122 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 1.54 (s, 9 H, *t*Bu), 2.49 (s, 3 H, CH_3), 2.73 (s, 3 H, CH_3), 8.40 (s, 1 H, 5-H) ppm. ^{13}C NMR[16a] ([D$_6$]acetone): δ = 16.6 (CH_3), 22.6 (CH_3), 25.7 (C*Me*$_3$), 62.9 (*C*Me$_3$), 126.0 (C-3), 130.3 (C-6), 137.6 (C-5), 143.5 (C-4), 148.1 (C-2) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −64 ($\Delta\nu_{1/2}$ = 90 Hz, N→O), −154 ($\Delta\nu_{1/2}$ = 170 Hz, -*N*$^+$≡N) ppm. IR (KBr): $\tilde{\nu}$ = 1500 cm^{-1} [N(O)=N], 2310 (N_2^+). $C_{12}H_{16}BBrF_4N_4O$ (398.99): calcd. C 36.12, H 4.04, N 14.04; found C 35.89, H 4.00, N 14.43.

4,6-Dibromo-2-(*tert*-butyl-*NNO*-azoxy)-5-methylphenyldiazonium Tetrafluoroborate (2e): Light-yellow solid (560 mg, 85 %), m.p. 111−115 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 1.51 (s, 9 H, *t*Bu), 2.47 (s, 3 H, CH_3), 8.78 (s, 1 H, 3-H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 20.4 (CH_3), 25.5 (C*Me*$_3$), 62.1 (*C*Me$_3$), 130.5 (C-3) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −60 ($\Delta\nu_{1/2}$ = 100 Hz, N→O), −156 ($\Delta\nu_{1/2}$ = 190 Hz, -*N*$^+$≡N) ppm. IR (KBr): $\tilde{\nu}$ = 1510 cm^{-1} [N(O)=N], 2300 (N_2^+). $C_{11}H_{13}BBr_2F_4N_4O$ (463.86): calcd. C 28.48, H 2.82, N 12.08; found C 28.39, H 2.83, N 12.04.

4-Bromo-2-(*tert*-butyl-*NNO*-azoxy)phenyldiazonium Tetrafluoroborate (2f):[6] Light brownish solid (470 mg, 89 %), m.p. 130−135 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 1.52 (s, 9 H, *t*Bu), 8.52 (dd, *J* = 8.8, 2.1 Hz, 1 H, 5-H), 8.87 (d, *J* = 2.1 Hz, 1 H, 3-H), 8.88 (d, *J* = 8.8 Hz, 1 H, 6-H) ppm. ^{13}C NMR[16a−16c] (273 K, [D$_6$]acetone): δ = 25.1 (C*Me*$_3$), 62.0 (*C*Me$_3$), 109.7 (C-1, $^3J_{3\text{-H}}$ = 9.0, $^3J_{5\text{-H}}$ = 11.8 Hz), 130.2 (C-3, ^3J = 6.0 Hz), 137.4 (C-6), 137.8 (C-5), 138.3 (C-4), 146.7 (C-2) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −67 ($\Delta\nu_{1/2}$ = 100 Hz, N→O), −151 ($\Delta\nu_{1/2}$ = 250 Hz, −*N*$^+$≡N) ppm. IR (KBr): $\tilde{\nu}$ = 1500 cm^{-1} [N(O)=N], 2290 (N_2^+). $C_{10}H_{12}BBrF_4N_4O$ (370.94): calcd. C 32.38, H 3.26, N 15.10; found C 32.45, H 3.30, N 14.99.

4,5-Dibromo-2-(*tert*-butyl-*NNO*-azoxy)phenyldiazonium Tetrafluoroborate (2g): Colorless solid (550 mg, 88 %), m.p. 102−106 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 1.51 (s, 9 H, *t*Bu), 8.56 (s, 1 H, 6-H), 8.91 (s, 1 H, 3-H) ppm. ^{13}C NMR[16a] ([D$_6$]acetone): δ = 25.3 (C*Me*$_3$), 62.4 (*C*Me$_3$), 110.5 (C-1), 130.5 (C-5), 131.6 (C-3), 139.5 (C-6), 141.8 (C-4), 145.3 (C-2) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −65 ($\Delta\nu_{1/2}$ = 80 Hz, N→O), −155 ($\Delta\nu_{1/2}$ = 190 Hz, −*N*$^+$≡N) ppm. IR (KBr): $\tilde{\nu}$ = 1500 cm^{-1} [N(O)=N], 2300 (N_2^+). $C_{10}H_{11}BBr_2F_4N_4O$ (449.83): calcd. C 26.70, H 2.46, N 12.46; found C 26.72, H 2.50, N 12.41.

6-Bromo-2-(*tert*-butyl-*NNO*-azoxy)-4-methylphenyldiazonium Tetrafluoroborate (2h): Colorless solid (520 mg, 95 %), m.p. 82−85 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 1.43 (s, 9 H, *t*Bu), 2.72 (s, 3 H, CH_3), 8.05 (d, *J* = 2 .1 Hz, 1 H, 3-H), 8.88 (d, *J* = 8.8 Hz, 1 H, 6-H) ppm. ^{13}C NMR[16a] ([D$_6$]acetone): δ = 21.5 (CH_3), 25.1 (C*Me*$_3$), 62.0 (*C*Me$_3$), 109.7 (C-1), 130.2 (C-3), 137.4 (C-6), 137.8 (C-5), 138.3 (C-4), 146.7 (C-2) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −67 ($\Delta\nu_{1/2}$ = 210 Hz, N→O), −151 ($\Delta\nu_{1/2}$ = 490 Hz, −*N*$^+$≡N) ppm. IR (KBr): $\tilde{\nu}$ = 1500 cm^{-1} [N(O)=N], 2290 (N_2^+). $C_{11}H_{14}BBrF_4N_4O$ (384.96): calcd. C 34.32, H 3.67, N 14.55; found C 34.01, H 3.72, N 14.33.

5-Bromo-2-(*tert*-butyl-*NNO*-azoxy)phenyldiazonium Tetrafluoroborate (2i): Colorless solid (480 mg, 90 %), m.p. 130−134 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 1.53 (s, 9 H, *t*Bu), 8.47 (d, *J* = 9.2 Hz, 1 H, 3-H), 8.94 (dd, *J* = 9.2, 1.9 Hz, 1 H, 4-H), 9.31 (d, *J* = 1.9 Hz, 1 H, 6-H) ppm. ^{13}C NMR[16c] ([D$_6$]acetone): δ = 25.34 (C*Me*$_3$), 61.5 (*C*Me$_3$), 134.0 (C-3), 136.9 (C-6), 146.0 (C-4) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −65 ($\Delta\nu_{1/2}$ = 50 Hz, N→O), −150 ($\Delta\nu_{1/2}$ = 220 Hz, −*N*$^+$≡N) ppm. IR (KBr): $\tilde{\nu}$ = 1500 cm^{-1} [N(O)=N], 2280 (N_2^+). $C_{10}H_{12}BBrF_4N_4O$ (370.94): calcd. C 32.38, H 3.26, N 15.10; found C 32.35, H 3.26, N 14.49.

4,6-Dibromo-2-(isopropyl-*NNO*-azoxy)phenyldiazonium Tetrafluoroborate (2v): Colorless solid (690 mg, 92 %), m.p. 179−182 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 1.37 (d, *J* = 6.6 Hz, 6 H, CH_3), 4.45 (h, *J* = 6.6 Hz, 1 H, CH), 8.93 (d, *J* = 1.6 Hz, 1 H, 3-H), 8.95 (d, *J* = 1.6 Hz, 1 H, 5-H) ppm. ^{13}C NMR[16a] ([D$_6$]acetone): δ = 19.3 (CH_3), 54.8 (CH), 112.9 (C-1), 129.7 (C-3), 131.0

(C-6), 138.9 (C-4), 141.7 (C-5), 147.4 (C-2) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −68 (Δν$_{1/2}$ = 80 Hz, N→O), −154 (Δν$_{1/2}$ = 200 Hz, $-N^+\equiv$N) ppm. IR (KBr): ν̃ = 1490 cm^{-1} [N(O)=N], 2290 (N_2^+). $C_9H_9BBr_2F_4N_4O$ (435.81): calcd. C 28.80, H 2.08, N 12.86; found C 28.63, H 2.09, N 12.65.

2-(Adamantan-1-yl-*NNO*-azoxy)-4,6-dibromophenyldiazonium Tetrafluoroborate (2w): Colorless solid (810 mg, 90 %), m.p. 152−154 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 1.87 (m, 6 H), 2.17 (m, 3 H), 2.26 (m, 6 H), 8.92 (d, *J* = 1.8 Hz, 1 H, 3-H), 9.17 (d, *J* = 1.8 Hz, 1 H, 5-H) ppm. ^{13}C NMR[16a] ([D$_6$]acetone): δ = 30.6, 37.6, 42.6, 128.3 (C-3), 138.7 (C-5) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −67 (Δν$_{1/2}$ = 40 Hz, N→O), −153 (Δν$_{1/2}$ = 220 Hz, $-N^+\equiv$N) ppm. IR (KBr): ν̃ = 1500 cm^{-1} [N(O)=N], 2270 (N_2^+). $C_{16}H_{17}BBr_2F_4N_4O$ (527.95): calcd. C 36.40, H 3.25, N 10.61; found C 36.50, H 3.26, N 10.35.

Transformation of Salts 2 into Compounds 3−5. ^{1}H NMR Monitoring: Solutions of diazonium salts **2a**, **2b**, **2d**−**i**, or cyclic salt **3c** in CD_3CN (10−20 mg/mL) or [D$_6$]acetone were monitored by ^{1}H NMR and ^{14}N NMR. The reaction conditions and yields are listed in Table 1.

2-(*tert*-Butyl)-1,2,3,4-benzotetrazin-2-ium 4-Oxide Tetrafluoroborate (3a): ^{1}H NMR (CD_3CN): δ = 1.98 (s, 9 H, *t*Bu), 8.6−8.8 (m, 4 H, Ar) ppm. ^{13}C NMR[16a−16e] (273 K, CD_3CN): δ = 28.9 (CH_3), 85.8 (C*Me*$_3$), 120.1 (C-5, ^2J = 2.2, ^3J = 6.0 Hz), 132.1 (C-8, ^2J = 1.5, ^3J = 6.0 Hz), 132.4 (br., C-4a), 142.8 (C-7, ^2J = 1.3, ^3J = 8.0 Hz), 143.0 (C-8a, ^3J = 5.4, ^3J = 9.7 Hz), 145.6 (C-6, ^3J = 8.3 Hz) ppm. ^{14}N NMR (CD_3CN): δ = −46 (Δν$_{1/2}$ = 100 Hz, N→O) ppm.

6,8-Dibromo-2-(*tert*-butyl)-1,2,3,4-benzotetrazin-2-ium 4-Oxide Tetrafluoroborate (3b). Method 1: A solution of diazonium salt **2b** (450 mg, 1 mmol) in dry MeCN (50 mL) was allowed to stand at 20 °C for 10 min. The solvent was then evaporated in vacuo (at 0 °C) and the residue was washed with cold CH_2Cl_2 and dried in vacuo to give **3b** (310 mg, 69 %) as bright yellow crystals, m.p. 127−133 °C (decomp.).

Method 2: Crystals of diazonium salt **2b** (450 mg, 1 mmol) were allowed to stand at 40 °C for 12 h. The residue was then washed with acetone and dried in vacuo to give **3b** (250 mg, 56 %), identical to the previous sample. ^{1}H NMR ([D$_6$]acetone): δ = 2.08 (s, 9 H, *t*Bu), 9.02 (d, *J* = 1.9 Hz, 1 H, 5-H), 9.27 (d, 1 H, 7-H) ppm. ^{13}C NMR[16b][16e] (273 K, [D$_6$]acetone): δ = 27.9 (CH_3), 85.8 (C*Me*$_3$), 122.1 (C-5, ^3J = 5.5 Hz), 128.4 (C-8, ^2J = 5.0 Hz), 134.3 (br., C-4a), 141.5 (C-6, ^2J = 4.0 Hz), 145.4 (C-8a), 148.6 (C-7, ^3J = 6.0 Hz) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −52 (Δν$_{1/2}$ = 60 Hz, N→O) ppm. IR (KBr): ν̃ = 1460 cm^{-1}. $C_{10}H_{11}BBr_2F_4N_4O$ (449.83): calcd. C 26.70, H 2.46, N 12.46; found C 26.71, H 2.44, N 12.70.

6,7,8-Tribromo-2-*tert*-butyl-1,2,3,4-benzotetrazin-2-ium 4-Oxide Tetrafluoroborate (3c): This compound was obtained from aniline **1c** by the general diazotization procedure. Bright yellow solid, m.p. 117−122 °C (decomp.). ^{1}H NMR (CD_3CN): δ = 2.10 (s, 9 H, *t*Bu), 9.00 (s, 1 H, 5-H) ppm. ^{14}N NMR (CD_3CN): δ = −54 (Δν$_{1/2}$ = 80 Hz, N→O) ppm. IR (KBr): ν̃ = 1470 cm^{-1}. $C_{10}H_{10}BBr_3F_4N_4O$ (528.73): calcd. C 22.72, H 1.91, N 10.60; found C 22.34, H 1.90, N 10.45.

8-Bromo-2-*tert*-butyl-5,6-dimethyl-1,2,3,4-benzotetrazin-2-ium 4-Oxide Tetrafluoroborate (3d): ^{1}H NMR ([D$_6$]acetone): δ = 2.1 (s, 9 H, *t*Bu), 2.83 (br. s, 6 H, 2 CH_3); 8.89 (s, 1 H, 5-H) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −48 (Δν$_{1/2}$ = 60 Hz, N→O) ppm.

6,8-Dibromo-2-*tert*-butyl-7-dimethyl-1,2,3,4-benzotetrazin-2-ium 4-Oxide Tetrafluoroborate (3e): A solution of diazonium salt **2e** (60 mg, 0.13 mmol) in dry MeCN (6 mL) was allowed to stand at 5 °C for 4 hours. The solvent was then evaporated in vacuo (at 0 °C) and the residue was washed with cold Et_2O and dried in vacuo to give **3e** (37 mg, 62 %) as a bright yellow solid, m.p. 130−135 °C (decomp.). ^{1}H NMR at 273 K ([D$_6$]acetone): δ = 2.08 (s, 9 H, *t*Bu), 3.16 (s, 3 H, CH_3), 9.10 (s, 1 H, 8-H) ppm. ^{13}C NMR[16a] (273 K, [D$_6$]acetone): δ = 26.3 (CH_3), 29.0 (C*Me*$_3$), 85.8 (*C*Me$_3$), 122.2 (C-5), 128.8 (C-8), 132.4 (C-4a), 141.5 (C-8a), 144.3 (C-6), 155.2 (C-7) ppm. ^{14}N NMR (273 K, [D$_6$]acetone): δ = −51 (Δν$_{1/2}$ = 120 Hz, N→O) ppm. IR (KBr): ν̃ = 1440 cm^{-1}. $C_{11}H_{13}BBr_2F_4N_4O$ (463.86): calcd. C 28.48, H 2.82, N 12.08; found C 28.31, H 2.83, N 12.51.

6-Bromo-2-*tert*-butyl-1,2,3,4-benzotetrazin-2-ium 4-Oxide Tetrafluoroborate (3f): Crystals of diazonium salt **2f** (370 mg, 1 mmol) were allowed to stand at 40 °C for 3 days. The residue was then washed with acetone and dried in vacuo to give **3f** (250 mg, 69 %) as colorless crystals, m.p. 129−133 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 2.06 (s, 9 H, *t*Bu), 8.96 (m, 2 H, 7-H and 8-H), 9.09 (dd, *J* = 1.6, 0.7 Hz, 1 H, 5-H) ppm. ^{13}C NMR[16a−16d] (273 K, [D$_6$]acetone): δ = 28.9 (C*Me*$_3$), 85.3 (*C*Me$_3$), 122.8 (C-5), 131.3 (br., C-4a), 133.3 (C-8), 141.4 (C-6, ^3J = 9.5, ^2J = 4.5 Hz), 142.4 (C-8a, $^3J_{7\text{-H}}$ = 9.5, $^3J_{5\text{-H}}$ = 5.1 Hz), 146.1 (C-7, ^3J = 6.2 Hz) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −51 (Δν$_{1/2}$ = 70 Hz) (N→O) ppm. IR (KBr): ν̃ = 1460 cm^{-1}. $C_{10}H_{12}BBrF_4N_4O$ (370.94): calcd. C 32.38, H 3.26, N 15.10; found C 32.42, H 3.21, N 15.43.

6,7-Dibromo-2-*tert*-butyl-1,2,3,4-benzotetrazinium 4-Oxide Tetrafluoroborate (3g): ^{1}H NMR (CD_3CN): δ = 1.97 (s, 9 H, *t*Bu), 8.99 (s, 1 H, 8-H), 9.13 (s, 1 H, 5-H) ppm. ^{14}N NMR (CD_3CN): δ = −48 (Δν$_{1/2}$ = 60 Hz, N→O).

8-Bromo-2-*tert*-butyl-6-methyl-1,2,3,4-benzotetrazinium 4-Oxide Tetrafluoroborate (3h): A solution of diazonium salt **2h** (100 mg, 0.26 mmol) in dry MeCN (9 mL) was allowed to stand at 5 °C for 2 hours. The solvent was then evaporated in vacuo (at 0 °C) and the residue was washed with cold Et_2O and dried in vacuo to give **3e** (85 mg, 85 %) as a yellow solid, m.p. 102−105 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 2.08 (s, 9 H, *t*Bu), 2.73 (s, 3 H, CH_3), 8.23 (d, J = 2.0 Hz, 1 H 5-H), 8.51 (d, J = 2.0 Hz, 1 H, 7-H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 22.2 (CH_3), 31.5 (C*Me*$_3$), 117.0, 143.3 ppm. ^{14}N NMR ([D$_6$]acetone): δ = −50 (Δν$_{1/2}$ = 50 Hz) (N→O) ppm. IR (KBr): ν̃ = 1450 cm^{-1}. $C_{11}H_{14}BBrF_4N_4O$ (384.96): calcd. C 34.32, H 3.67, N 14.55; found C 34.39, H 3.70, N 14.51.

7-Bromo-2-*tert*-butyl-1,2,3,4-benzotetrazin-2-ium 4-Oxide Tetrafluoroborate (3i): ^{1}H NMR (CD_3CN): δ = 2.07 (s, 9 H, *t*Bu), 8.37 (d, *J* = 2.0 Hz, 1 H, 8-H), 8.71 (d, *J* = 8.7 Hz, 1 H, 5-H), 9.40 (dd, *J* = 8.7, 2.0 Hz, 1 H, 6-H) ppm. ^{14}N NMR (CD_3CN): δ = −48 (Δν$_{1/2}$ = 60 Hz, N→O).

5,7-Dibromo-1,2,3,4-benzotetrazine 1-Oxide (4b), Procedure A: A solution of cyclic salt **3b** (450 mg, 1 mmol) in MeCN (45 mL) containing H_2O (0.4 mL) was allowed to stand at 5 °C for 2 days. The solution was then concentrated ca. 90 % in vacuo at a temperature of 0 °C, poured into water with ice, and extracted with cooled CH_2Cl_2. The extract was washed with ice-cold water and dried ($CaCl_2$). The solvent was evaporated in vacuo and the residue was washed with pentane and dried in vacuo to give 210 mg (60 %) of **4b**, m.p. 78−80 °C (decomp.). **Procedure B:** A solution of diazonium salt **2b** (110 mg, 0.25 mmol) in MeCN (2 mL) was mixed with silica gel (Aldrich, 70−270 mesh, 1 g) and the solvent was evaporated in vacuo. The residue was placed on a silica gel pad (1 g of SiO_2) and eluted with warm $CHCl_3$ (40 °C) over a period

of 15 min. The solution was collected in a well cooled flask, and the solvent was then evaporated in vacuo at a temperature of 0 °C. The residue was washed with pentane to give 42 mg (55 %) of **4b** identical to the sample obtained above, m.p. 78−80 °C (decomp.). ^{1}H NMR[5] ([D$_6$]acetone): δ = 8.66 (d, J = 1.8 Hz, 1 H, 8-H), 8.87 (d, 1 H, 6-H) ppm. ^{13}C NMR[16a][16b][16d] ([D$_6$]acetone): δ = 121.0 (C-8, ^1J = 181, ^3J = 5.4 Hz), 125.4 (C-5, ^2J = 4.5, ^4J = 1.7 Hz), 131.2 (C-7, ^2J = 4.0 Hz), 132.7 (br., C-8a), 140.4 (C-4a, ^3J = 7.4, ^3J = 4.9 Hz), 144.1 (C-6, ^1J = 177, ^3J = 6.5 Hz). ^{14}N NMR ([D$_6$]acetone): δ = −52 (Δν$_{1/2}$ = 50 Hz, N→O) ppm. MS (70 eV): *m*/*z* (relative intensities) = 276, 278, 280 (1:2:1) [M$^+$ − N$_2$]. $C_6H_2Br_2N_4O$ (305.91): calcd. C 23.56, H 0.66, N 18.31; found C 23.44, H 0.61, N 18.48.

5,6,7-Tribromo-1,2,3,4-benzotetrazine 1-Oxide (4c): The cyclic salt **3c** (210 mg, 0.39 mmol) was dissolved in MeCN (20 mL) at 0 °C and the solution was allowed to stand at 20 °C for 1 h. The solvent was then evaporated in vacuo (−5 °C) and the residue was purified by chromatography (silica gel, benzene) to yield 30 mg (20 %) of **4c** as a bright yellow solid, m.p. 62−66 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 8.82 (s, 1 H, 8-H) ppm. ^{13}C NMR[16a] ([D$_6$]acetone): δ = 122.3 (C-8), 128.3 (C-5), 133.4 (C-7), 139.3 (C-6, ^3J = 6.3 Hz) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −54 (Δν$_{1/2}$ = 80 Hz, N→O) ppm. MS (70 eV): *m*/*z* (relative intensities) = 353, 355, 357, 359, 361 (1:3:5:3:1) [M$^+$ − N$_2$]. $C_6HBr_3N_4O$ (384.81): calcd. C 18.73, H 0.26, Br 62.29, N 14.56; found C 18.72, H 0.26, Br 62.12, N 15.02.

5-Bromo-7,8-dimethyl-1,2,3,4-benzotetrazine 1-Oxide (4d): A solution of diazonium salt **2d** (220 mg, 0.55 mmol) in MeCN (25 mL) containing H_2O (0.2 mL) was allowed to stand at 20 °C for 2 h. The solution was then poured into water with ice and extracted with cooled CH_2Cl_2. The extract was washed with ice-cold water and dried ($CaCl_2$). The solvent was evaporated in vacuo and the residue was washed with pentane and dried in vacuo to give 70 mg (50 %) of **4d** as yellow crystals, m.p. 125−130 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 2.56 (s, 3 H, CH_3), 2.84 (s, 3 H, CH_3), 8.21 (s, 1 H, 6-H) ppm. ^{13}C NMR [16a] ([D$_6$]acetone): δ = 18.0 (CH_3), 24.2(CH_3), 123.2 (C-5), 126.6 (C-8, ^3J = 6.0 Hz), 140.4 (C-7), 146.9 (C-6) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −47 (Δν$_{1/2}$ = 50 Hz, N→O) ppm. MS (70 eV): *m*/*z* (relative intensities) = 254, 256 (1:1) [M$^+$ − N$_2$]. $C_8H_7BrN_4O$ (255.07): calcd. C 37.67, H 2.77, Br 31.33, N 21.97; found C 37.72, H 2.69, Br 30.98, N 21.13.

5,7-Dibromo-6-methyl-1,2,3,4-benzotetrazine 1-Oxide (4e): A solution of cyclic salt **3e** (150 mg, 0.3 mmol) in MeCN (15 mL) containing H_2O (0.15 mL) was allowed to stand at 0 °C for 2 days. The solution was then concentrated ca. 90 % in vacuo at a temperature of 0 °C, poured into water with ice, and extracted with cooled CH_2Cl_2. The extract was washed with ice-cold water and dried ($MgSO_4$). The solvent was evaporated in vacuo, and the residue was purified by chromatography (silica gel, benzene) to yield 11 mg (10 %) of **4e**, m.p. 71−75 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 2.96 (s, 3 H, Me); 8.66 (s, 1 H, 8-H) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −52 (Δν$_{1/2}$ = 50 Hz, N→O) ppm. MS (70 eV): *m*/*z* (relative intensities) = 290, 292, 294 (1:2:1) [M$^+$ − N$_2$]. $C_7H_4Br_2N_4O$ (319.94): calcd. C 26.28, H 1.26, Br 49.95, N 17.51; found C 26.34, H 1.26, Br 50.03, N 17.45.

7-Bromo-1,2,3,4-benzotetrazine 1-Oxide (4f): ^{1}H NMR ([D$_6$]acetone): δ = 8.46 (dd, J = 8.7, 2.0 Hz, 1 H, 6-H), 8.61 (d, J = 2.0 Hz, 1 H, 8-H), 8.68 (d, J = 8.7 Hz, 1 H, 5-H) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −51 (Δν$_{1/2}$ = 110 Hz, N→O) ppm.

6,7-Dibromo-1,2,3,4-benzotetrazine 1-Oxide (4g): ^{1}H NMR (CD_3CN): δ = 8.71 (s, 1 H, 5-H), 8.81 (s, 1 H, 8-H) ppm. ^{14}N NMR (CD_3CN): δ = −48 (Δν$_{1/2}$ = 60 Hz, N→O) ppm.

5-Bromo-7-(4-morpholinyl)-1,2,3,4-benzotetrazine 1-Oxide (4o): Morpholine (0.25 mL) was added to a solution of BTO **4b** (270 mg, 0.88 mmol) in dry MeCN (25 mL). After 30 min stirring at 20 °C, the solvent was evaporated in vacuo ($T \leq 20$ °C). The residue was washed with cold MeOH (5 mL), Et_2O (2×10 mL), and pentane (2×10 mL), and then dried in vacuo to give 150 mg (54 %) of **4o** as bright red crystals, m.p. 135−137 °C (decomp.). ^{1}H NMR ([D$_6$]DMSO): δ = 3.18 (m, 4 H, CH_2N), 3.71 (m, 4 H, CH_2O), 7.21 (d, J = 2.1 Hz, 1 H, 6-H), 8.90 (d, J = 2.1 Hz, 1 H, 8-H) ppm. ^{14}N NMR ([D$_6$]DMSO): δ = −57 (Δν$_{1/2}$ = 50 Hz, N→O) ppm. MS (70 eV): *m*/*z* (relative intensities) = 283, 285 (1:1) [M$^+$ − N$_2$]. $C_{10}H_{10}BrN_5O_2$ (312.12): calcd. C 38.48, H 3.23, Br 25.60, N 22.44; found C 38.33, H 3.18, Br 26.12, N 22.03.

5-Bromo-7-dimethylamino-1,2,3,4-benzotetrazine 1-Oxide (4p): Aqueous dimethylamine (33 %, 3 mL) was added to a solution of BTO **4b** (210 mg, 0.68 mmol) in MeCN (10 mL). After 40 min stirring at 20 °C, workup was accomplished in the same way as for **4o** to give 120 mg (65 %) of **4p** as bright red crystals, m.p. 138−142 °C (decomp.). ^{1}H NMR ([D$_6$]DMSO): δ = 3.23 (s, 6 H, CH_3), 6.89 (d, J = 2.0 Hz, 1 H, 6-H), 8.14 (d, J = 2.0 Hz, 1 H, 8-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 40.3 (Me), 89.9, 124.1, 127.9, 131.6, 133.3, 153.9 ppm. ^{14}N NMR ([D$_6$]DMSO): δ = −59 (Δν$_{1/2}$ = 200 Hz, N→O), −367 (Δν$_{1/2}$ = 500 Hz, NMe_2) ppm. MS (70 eV): *m*/*z* (relative intensities) = 241, 243 (1:1) [M$^+$ − N$_2$]. $C_8H_8BrN_5O$ (270.09): calcd. C 35.58, H 2.99, Br 29.58, N 25.93; found C 35.48, H 2.90, Br 29.81, N 25.98.

5-Bromo-7-diethylamino-1,2,3,4-benzotetrazine 1-Oxide (4q): Diethylamine (1 mL) was added to a solution of BTO **4b** (500 mg, 1.63 mmol) in dry MeCN (30 mL). After 30 min stirring at 20 °C, workup was accomplished in the same way as for **4o** to give 310 mg (63 %) of **4q** as bright red crystals, m.p. 142−144 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 2.05 (t, J = 6.7 Hz, 6 H, CH_3), 3.76 (q, J = 6.7 Hz, 4 H, CH_2), 7.07 (d, J = 2.1 Hz, 1 H, 6-H), 8.10 (d, J = 2.1 Hz, 1 H, 8-H) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −58 (Δν$_{1/2}$ = 40 Hz, N→O), −327 (Δν$_{1/2}$ = 180 Hz, NEt_2) ppm. MS (70 eV): *m*/*z* (relative intensities) = 269, 271 (1:1) [M$^+$ − N$_2$]. $C_{10}H_{12}BrN_5O$ (298.14): calcd. C 40.29, H 4.06, Br 26.80, N 23.49; found C 40.13, H 4.09, Br 26.83, N 23.31.

5-Bromo-7-methoxy-1,2,3,4-benzotetrazine 1-Oxide (4r): A solution of MeONa, obtained from sodium (10 mg) and dry MeOH (1.5 mL), was added to a stirred and cooled (−20 °C) solution of BTO **4b** (135 mg, 0.44 mmol) in dry MeOH (7 mL). After 2 h stirring at −20 °C, the temperature was brought to 20 °C. The reaction mixture was neutralized with dilute aqueous HCl, the solvent was evaporated in vacuo, and the residue was purified by chromatography (silica gel, benzene) to give 60 mg (52 %) of **4r** as light orange crystals, m.p. 103−105 °C (decomp.). ^{1}H NMR ([D$_6$]DMSO): δ = 4.09 (s, 3 H, OMe), 7.63 (d, J = 2.2 Hz, 1 H, 6-H), 8.35 (d, J = 2.2 Hz, 1 H, 8-H) ppm. ^{13}C NMR[16a,16b] ([D$_6$]DMSO): δ = 57.7 (Me), 95.7 (C-8), 124.1 (C-5), 132.4 (C-8a), 132.5 (C-6), 136.4 (C-4a), 164.9 (C-7). ^{4}N NMR ([D$_6$]DMSO): δ = −50 (Δν$_{1/2}$ = 60 Hz, N→O) ppm. MS (70 eV): *m*/*z* (relative intensities) = 228, 230 (1:1) [M$^+$ − N$_2$]. $C_7H_5BrN_4O_2$ (257.04): calcd. C 32.71, H 1.96, Br 31.09, N 21.80; found C 32.77, H 1.92, Br 29.92, N 21.83.

5-Methoxy-7,8-dimethyl-1,2,3,4-benzotetrazine 1-Oxide (4s): A solution of MeONa, obtained from sodium (9 mg) and dry MeOH (1 mL), was added with stirring and cooling (−20 °C) to a solution of BTO **4d** (40 mg, 0.17 mmol) in dry MeOH (2 mL), and stirring at this temperature was continued for 6 h. The reaction mixture was worked up as described for **4r** and the residue was purified by

chromatography (silica gel, $CHCl_3$) to give 13 mg (40 %) of **4s** as light yellow crystals, m.p. 71−74 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 2.51 (s, 3 H, CH_3), 2.78 (s, 3 H, CH_3), 4.14 (s, 3 H, OCH_3), 8.48 (s, 1 H, 6-H) ppm. ^{14}N NMR ($CDCl_3$): δ = −49 ($\Delta\nu_{1/2}$ = 50 Hz) ppm. MS (70 eV): *m/z* = 178 [$M^+ - N_2$]. $C_9H_{10}N_4O_2$ (206.20): calcd. C 52.42, H 4.89, N 27.17; found C 52.53, H 4.92, N 26.93.

Treatment of BTO 4c with MeONa: A solution of MeONa, obtained from sodium (5 mg) and dry MeOH (1 mL), was added to a stirred and cooled (−20 °C) solution of BTO **4c** (25 mg, 0.064 mmol) in dry MeOH (1.5 mL) and the stirring at this temperature was continued for 20 min. Workup was accomplished as described for **4r**. Chromatographic separation (silica gel, $CHCl_3$) gave 6.9 mg (31 %) of BTO **4v** and 4.7 mg (22 %) of **5w**.

5,6-Dibromo-7-methoxy-1,2,3,4-benzotetrazine 1-Oxide (4v): Light orange crystals, m.p. 92−94 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 3.84 (s, 3 H, OMe), 7.32 (s, 1 H, 6-H) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −53 ($\Delta\nu_{1/2}$ = 60 Hz, N→O) ppm. MS (70 eV): *m/z* (relative intensities) = 306, 308, 310 (1:2:1) [$M^+ - N_2$]. $C_7H_4Br_2N_4O_2$ (335.94): calcd. C 25.03, H 1.20, Br 47.57, N 16.68; found C 25.16, H 1.19, Br 47.35, N 16.33.

2-Azido-3,5-dibromo-4-methoxy-1-nitrosobenzene (5w): Yellow-orange crystals, m.p. 114−116 °C (decomp.). ^{1}H NMR ([D$_6$]acetone): δ = 4.25 (s, 3 H, OMe), 6.46 (s, 1 H, 6-H) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −144 ($\Delta\nu_{1/2}$ = 90 Hz, −N=N^+=N^-) ppm. MS (70 eV): *m/z* (relative intensities) = 306, 308, 310 (1:2:1) [$M^+ - N_2$] ppm. IR (KBr): $\tilde{\nu}$ = 2100, 2140 w cm^{-1} (N_3). $C_7H_4Br_2N_4O_2$ (335.94): calcd. C 25.03, H 1.20, Br 47.57, N 16.68; found C 25.18, H 1.23, Br 47.31, N 16.29.

2-Azido-3,5-dibromo-1-nitrosobenzene (5b): A solution of BTO **4b** (200 mg, 0.65 mmol) in MeCN (20 mL) was allowed to stand at 20 °C for 2 h. The solvent was then evaporated in vacuo and the residue was extracted with pentane. The extract was evaporated in vacuo (0 °C) to give 80 mg (40 %) of **5b** as a yellow solid, m.p. 54−57 °C (decomp.). ^{1}H NMR[5] ([D$_6$]acetone): δ = 6.23 (d, *J* = 2.2 Hz, 1 H, 6-H), 8.20 (d, 1 H, 4-H) ppm. ^{13}C NMR[16b] ([D$_6$]acetone): δ = 110.1 (C-6), 118.5 (C-5), 119.2 (C-3), 143.1 (C-4), 145.4 (C-2), 159.0 (C-1) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −143 ($\Delta\nu_{1/2}$ = 100 Hz, −N=N^+=N^-) ppm. IR (KBr): $\tilde{\nu}$ = 2120, 2150 w cm^{-1} (N_3). MS (70 eV): *m/z* (relative intensities) = 276, 278, 280 (1:2:1) [$M^+ - N_2$]. $C_6H_2Br_2N_4O$ (305.91): calcd. C 23.56, H 0.66, Br 52.24, N 18.31; found C 23.64, H 0.67, Br 52.41, N 18.12.

2-Azido-3,4,5-tribromo-1-nitrosobenzene (5c): ^{1}H NMR ([D$_6$]acetone): δ = 6.50 (s, 1 H, 6-H) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −143 ($\Delta\nu_{1/2}$ = 60 Hz, N→O) ppm.

2-Azido-3,5-dibromo-4-methyl-1-nitrosobenzene (5e): ^{1}H NMR ([D$_6$]acetone): δ = 2.65 (s, 3 H, CH_3), 6.40 (s, 1 H, 6-H) ppm. ^{14}N NMR ([D$_6$]acetone): δ = −142 ($\Delta\nu_{1/2}$ = 60 Hz, N→O) ppm.

General Procedure for Decomposition of Diazonium Tetrafluoroborates 2 to Furazans 6: The solution of diazonium salt in MeCN was allowed to stand at a given temperature (see Table 1). The solvent was then evaporated and the residue was purified by chromatography on silica gel (eluent CH_2Cl_2).

Benzofurazan (6a): Decomposition of **2a** (100 mg) in MeCN (3 mL) afforded 35 mg (84 %) of **6a**, m.p. 53−55 °C, identical with an authentic sample.

4,6-Dibromobenzofurazan (6b) from Salt 2b: Decomposition of **2b** (200 mg) in MeCN (4 mL) afforded 120 mg (95 %) of **6b**, m.p. 112−115 °C (from CH_2Cl_2) (ref.[17] m.p. 113 °C). ^{1}H NMR ([D$_6$]acetone): δ = 7.98 (d, *J* = 1.4 Hz, 1 H, 5-H), 8.32 (d, 1 H, 7-H) ppm. ^{13}C NMR[16c] ([D$_6$]acetone): δ = 110.7 (C-4), 118.7 (C-7), 126.6 (C-6), 138.6 (C-5), 149.5 (C-3a), 150.6 (C-7a) ppm.

Decomposition of 2w with Formation of 4,6-Dibromobenzofurazan (6b). Procedure 1: A solution of **2w** in CD_3CN (40 mg/mL) was monitored by ^{1}H NMR. After 10 days, 85 % of unchanged salt **2w** and 15 % of **6b** were observed. **Procedure 2:** A solution of diazonium salt **2w** (50 mg, 0.095 mmol) in MeCN (2 mL) was heated under reflux for 5 h. The solution was then brought to room temperature and the solvent was evaporated. The residue was purified by chromatography (silica gel, benzene) to give 16 mg (60 %) of **6b**, identical to the sample obtained from **2b**.

4,5,6-Tribromobenzofurazan (6c): Decomposition of **2c** (53 mg) in MeCN (10 mL) afforded 33 mg (92 %) of **6c**, m.p. 148−150 °C. ^{1}H NMR ($CDCl_3$): δ = 8.27 (s, 1 H, 7-H) ppm. ^{13}C NMR[16a] ($CDCl_3$): δ = 113.0 (C-4), 118.7 (C-7), 129.6 (C-5), 132.5 (C-6), 147.7 (C-7a), 149.5 (C-3a) ppm. MS (70 eV): *m/z* (relative intensities) = 352, 354, 356, 358, 360 (1:3:5:3: 1) [M^+]. $C_6HBr_3N_2O$ (356.80): calcd. C 20.20, H 0.28, Br 67.18, N 7.85; found C 20.15, H 0.29, Br 67.43, N 7.90.

4-Bromo-6,7-dimethylbenzofurazan (6d): Decomposition of **2d** (80 mg) in MeCN (2 mL) afforded 34 mg (80 %) of **6d**, m.p. 114−116 °C. ^{1}H NMR ([D$_6$]acetone): δ = 2.43 (s, 3 H, Me), 2.55 (s, 3 H, Me), 7.71 (s, 1 H, 5-H) ppm. MS (70 eV): *m/z* (relative intensities) = 226, 228 (1:1) [M^+]. $C_8H_7BrN_2O$ (227.06): calcd. C 42.32, H 3.11, Br 35.19, N 12.34; found C 42.19, H 3.13, Br 35.51, N 12.29.

4,6-Bromo-5-methylbenzofurazan (6e): Decomposition of **2e** (40 mg) in MeCN (2 mL) afforded 18 mg (85 %) of **6e,** m.p. 84−86 °C. ^{1}H NMR ([D$_6$]acetone): δ = 2.71 (s, 3 H, Me), 8.42 (s, 1 H, 7-H) ppm. MS (70 eV): *m/z* (relative intensities) = 290, 292, 294 (1:2:1) [M^+]. $C_7H_4Br_2N_2O$ (291.93): calcd. C 28.80, H 1.38, Br 54.74, N 9.60; found C 28.87, H 1.37, Br 54.69, N 9.49.

5-Bromobenzofurazan (6f) from Salt 2f: Decomposition of **2f** (200 mg) in MeCN (4 mL) afforded 100 mg (90 %) of **6f**, m.p. 74−76 °C (from CH_2Cl_2) (ref.[18] 75 °C).

5-Bromobenzofurazan (6f) from Salt 2i: Decomposition of **2i** (110 mg) in MeCN (5 mL) afforded 48 mg (80 %) of **6f**, identical to the sample obtained from salt **2f**.

5,6-Dibromobenzofurazan (6g): Decomposition of **2g** (90 mg) in MeCN (9 mL) afforded 46 mg (90 %) of **6g**, m.p. 87−89 °C (ref.[19] 87−87.5 °C).

4-Bromo-6-methylbenzofurazan (6h): Decomposition of **2h** (120 mg) in MeCN (3 mL) afforded 51 mg (75 %) of **6g**, m.p. 69−71 °C. ^{1}H NMR ([D$_6$]acetone): δ = 2.52 (s, 3 H, Me), 7.71 (d, *J* = 1.8 Hz, 1 H, 7-H), 7.78 (d, *J* = 1.8 Hz, 1 H, 5-H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 22.0 (Me), 113.5 (C-7), 138.9 (C-5) ppm. MS (70 eV): *m/z* (relative intensities) = 212, 214 (1:1) [M^+]. $C_7H_5BrN_2O$ (213.03): calcd. C 39.47, H 2.37, Br 37.51, N 13.15; found C 39.91, H 2.33, Br 37.55, N 12.95.

General Procedure for Decomposition of Diazonium Tetrafluoroborates 2j−n Obtained in situ: Diazonium tetrafluoroborates **2** were obtained in situ by the general diazotization reaction and the reaction mixture was allowed to stand at a given temperature (see Table 1). The solvent was then evaporated and the residue was purified by chromatography on silica gel (eluent $CHCl_3$ or CH_2Cl_2).

5-Nitrobenzofurazan (6j): Aniline **1j** gave 140 mg (60 %) of **6j** as a colorless solid, m.p. 64−66 °C (from CH_2Cl_2) (ref.[20] 65−66 °C).

4-Nitrobenzofurazan (6k): Aniline **1k** gave 160 mg (70 %) of **6k** as a colorless solid, m.p. 95−97 °C (ref.[21] 96.5−98 °C). Eluent for chromatography: benzene.

4-Bromo-6-nitrobenzofurazan (6l): Aniline **1l** gave 280 mg (82 %) of **6l** as a colorless solid, m.p. 104−106 °C. ^{1}H NMR ($CDCl_3$): δ = 8.46 (d, J = 2.0 Hz, 1 H, 5-H), 8.88 (d, J = 2.0 Hz, 1 H, 7-H) ppm. ^{14}N NMR ($CDCl_3$): δ = −16 ($\Delta\nu_{1/2}$ = 100 Hz, NO_2) ppm. MS (70 eV): *m*/*z* (relative intensities) = 243, 245 (1:1) [M^+]. $C_6H_2BrN_3O_3$ (244.00): calcd. C 29.53, H 0.83, Br 32.75, N 17.22; found C 29.43, H 0.83, Br 32.54, N 17.23.

4,6-Dibromobenzofurazan (6b) from Aniline 1m: Aniline **1m** gave 260 mg (65 %) of **6b**, identical to a sample obtained from salt **2b**. Eluent for chromatography: benzene.

4,5,7-Tribromobenzofurazan (6n): Aniline **1n** gave 410 mg (80 %) of **6n** as a colorless solid, m.p. 121−123 °C (ref.[22] 121−125 °C). Eluent for chromatography: benzene.

4-Bromo-6-(4-morpholinyl)benzofurazan (6o): Morpholine (1 mL) was added to a solution of furazan **6b** (110 mg, 0.39 mmol) in dry MeCN (3 mL). After 1 day standing at 20 °C, the solvent was evaporated in vacuo and the residue was recrystallized from pentane to afford 100 mg (90 %) of **6o** as light yellow needles, m.p. 54−56 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 3.61 (m, 4 H, CH_2N), 3.80 (m, 4 H, CH_2O), 6.51 (d, J = 1.9 Hz, 1 H, 5-H), 7.54 (d, J = 1.9 Hz, 1 H, 7-H) ppm. ^{13}C NMR[16a] ([D$_6$]DMSO): δ = 48.7 (CH_2N), 65.6 (CH_2O), 105.7 (C-7) 111.2 (C-4), 128.1 (C-5), 139.5 (C-3a), 150.6 (C-6), 155.1 (C-7a) ppm. MS (70 eV): *m*/*z* (relative intensities) = 283, 285 (1:1) [M^+]. $C_{10}H_{10}BrN_3O_2$ (284.1): calcd. C 42.27, H 3.55, Br 28.12, N 14.79; found C 42.40, H 3.53, Br 28.41, N 14.71.

4-Bromo-6-dimethylaminobenzofurazan (6p): Me_2NH (0.5 mL) was added to a solution of furazan **6b** (70 mg, 0.25 mmol) in dry DMSO (5 mL). After 2 days standing at 20 °C, the solution was poured into water and extracted with Et_2O. The extract was dried ($MgSO_4$), the solvent was evaporated in vacuo, and the residue was purified by chromatography (silica gel, benzene) to yield 55 mg (90 %) of **6p** as a yellow solid, m.p. 156−157 °C. ^{1}H NMR ([D$_6$]DMSO): 3.23 (s, 3 H, Me), 6.31 (br. s, 1 H, 5-H), 7.25 (br. s, 1 H, 7-H) ppm. MS (70 eV): *m*/*z* (relative intensities) = 241, 243 (1:1) [M^+]. $C_8H_8BrN_3O$ (242.07): calcd. C 39.69, H 3.33, Br 33.01, N 17.36; found C 39.54, H 3.33, Br 33.00, N 17.45.

4-Bromo-6-diethylaminobenzofurazan (6q): Et_2NH (1 mL) was added to a solution of furazan **6b** (150 mg, 0.54 mmol) in dry DMSO (10 mL). After 2 days standing at 20 °C, the reaction mixture was worked up as described for **6p** and the residue was purified by chromatography (silica gel, $CHCl_3$) to yield 125 mg (86 %) of **6q** as a light yellow solid, m.p. 78−81 °C. ^{1}H NMR ([D$_6$]acetone): 1.26 (t, J = 6.6 Hz, 6 H, CH_3), 3.80 (q, J = 6.6 Hz, 4 H, CH_2), 6.2 (br. s, 1 H, 5-H), 7.16 (br. s, 1 H, 7-H) ppm. ^{13}C NMR[16a] ([D$_6$]acetone): δ = 12.9 (CH_3), 47.0 (CH_2), 103.2 (C-7) 111.5 (C-4), 126.3 (C-5), 138.8 (C-3a), 149.1 (C-6), 152.6 (C-7a) ppm. MS (70 eV): *m*/*z* (relative intensities) = 269, 271 (1:1) [M^+]. $C_{10}H_{12}BrN_3O$ (270.13): calcd. C 44.46, H 4.48, Br 29.58, N 15.56; found C 44.44, H 4.53, Br 29.62, N 15.39.

4-Bromo-6-methoxybenzofurazan (6r): A solution of MeONa in MeOH (0.3 M, 2 mL) was added to a solution of furazan **6b** (150 mg, 0.53 mmol) in dry MeOH (5 mL). After 1 h stirring at 40−45 °C, the reaction mixture was neutralized with aqueous HCl, the solvent was evaporated in vacuo, and the residue was recrystallized from C_6H_6 to yield 97 mg (80 %) of **6r**, m.p. 86−87 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 3.78 (s, 3 H, Me), 6.82 (d, J = 2.1 Hz, 1 H, 5-H), 7.87 (d, J = 2.1 Hz, 1 H, 7-H) ppm. MS (70 eV): *m*/*z* (relative intensities) = 228, 230 (1:1) [M^+]. $C_7H_5BrN_2O_2$ (229.03): calcd. C 36.71, H 2.20, Br 34.89, N 12.23; found C 36.84, H 2.22, Br 34.57, N 12.31.

4-Methoxy-6,7-dimethylbenzofurazan (6s): A solution of MeONa in MeOH (0.1 M 1.5 mL) was added to a solution of furazan **6d** (20 mg, 0.1 mmol) in dry MeOH (2 mL). After 3 h at reflux, the reaction mixture was neutralized as in the previous case and the residue was chromatographed (silica gel, $CHCl_3$) to afford 12 mg (70 %) of **6s**, m.p. 72−74 °C. ^{1}H NMR ($CDCl_3$): δ = 2.24 (s, 3 H, Me), 2.30 (s, 3 H, Me), 4.16 (s, 3 H, OMe), 7.98 (s, 1 H, 5-H) ppm. MS (70 eV): *m*/*z* = 179 [M^+]. $C_9H_{10}N_2O_2$ (179.19): calcd. C 60.66, H 5.66, N 15.72; found C 60.56, H 5.63, N 15.91.

Treatment of 6c with MeONa: A solution of MeONa in MeOH (0.1 M, 0.4 mL) was added to a solution of furazan **6c** (40 mg, 0.12 mmol) in dry MeOH (6 mL). After 40 min stirring at 20 °C, the reaction mixture was neutralized as in the previous case and the residue was chromatographed (silica gel, $CHCl_3$) to afford 13 mg (35 %) of **6t** and 21 mg (60 %) of **6u**.

4,5-Bromo-6-methoxybenzofurazan (6t): M.p. 104−106 °C. ^{1}H NMR ([D$_6$]acetone): δ = 4.06 (s, 3 H, OMe), 8.46 (s, 1 H, 7-H) ppm. MS (70 eV): *m*/*z* (relative intensities) = 306, 308, 310 (1:2:1) [M^+]. $C_7H_4Br_2N_2O_2$ (307.93): calcd. C 27.30, H 1.31, Br 51.90, N 9.10; found C 27.40, H 1.30, Br 52.01, N 9.17.

4,6-Bromo-5-methoxybenzofurazan (6u): m.p. 93−95 °C. ^{1}H NMR ([D$_6$]acetone): δ = 4.50 (s, 3 H, OMe), 8.17 (s, 1 H, 7-H) ppm. MS (70 eV): *m*/*z* (relative intensities) = 306, 308, 310 (1:2:1) [M^+]. $C_7H_4Br_2N_2O_2$ (307.93): calcd. C 27.30, H 1.31, Br 51.90, N 9.10; found C 27.41, H 1.32, Br 51.77, N 9.03.

General Procedure for Decomposition of BTOs 4: Samples of BTOs **4b**−**e** and **4o**−**t** were dissolved in MeCN (concentration 15 mmol/L) and the reaction mixture was allowed to stand in a thermostat until the BTO disappeared (TLC monitoring). The time of decomposition is given in Table 2. BTOs **4f** and **4g** were unobtainable in a pure state. They was obtained in CD_3CN solution, the acidic impurities were then removed by filtration through a silica gel pad, and the concentration of BTO was adjusted to the standard value of 15 mmol/L (^{1}H NMR monitoring). After the decomposition was complete, the solvent was evaporated in vacuo, and the residue was chromatographed (silica gel, benzene or $CHCl_3$) to afford furazans **6** (Table 3). All furazans obtained were identical to the samples obtained above.

Table 3. The yields of furazans **6b**−**e** and **6o**−**t** obtained by decomposition of BTOs **4b**−**e** and **4o**−**t**

Starting BTO **4**	Furazan **6**	Yield [mg]	Yield [%]
4b	**6b**	40	93
4c	**6c**	51	95
4d	**6d**	31	92
4e	**6e**	37	85
4o	**6o**	38	90
4p	**6p**	33	90
4q	**6q**	36	90
4r	**6r**	30	87
4s	**6s**	22	83
4t	**6t**	42	90

Decomposition of Azide 5b to afford 4,6-Dibromobenzofurazan (6b): A solution of azide **5b** (30 mg, 0.1 mmol) in MeCN (10 mL) was allowed to stand at 20 °C for 30 min. The solvent was then evaporated in vacuo, and the residue was washed with 5 mL of pentane and dried to give 25.5 mg (92 %) of **6b**, identical to the sample obtained above.

Decomposition of Azide 5u to afford 4,6-Bromo-5-methoxybenzofurazan (6u): A solution of azide **5u** (7 mg, 0.022 mmol) in MeCN (2 mL) was allowed to stand for 20 min at 20 °C. The reaction mixture was worked up as described above to give 4.6 mg (71 %) of furazan **6u**, identical to the sample obtained above.

2-*tert*-Butyl-1,2,3,4-benzotetrazin-6(2*H*)-one 4-Oxide (8) from 3j: The diazonium salt **2j** was prepared from aniline **1j** (300 mg, 1.26 mmol) and $NOBF_4$ (180 mg, 1.5 mmol) at −20 °C in MeCN (5 mL). DMSO (1 mL) containing H_2O (0.1 mL, 5.6 mol) was added to this solution at −20 °C, and stirring was continued for 15 min at this temperature. The reaction mixture was worked up as described for **7**. The residue was purified by chromatography (silica gel, $CHCl_3$ and Et_2O consecutively) to yield 110 mg (40 %) of **8** as a deep red solid, m.p. 188−189 °C (decomp.), identical to a sample obtained from salt **3c**.[6]

2-(Adamantan-1-yl)-8-bromo-1,2,3,4-benzotetrazin-6(2*H*)-one 4-Oxide (9): The diazonium salt **2w** (42 mg, 0.08 mmol) was added with stirring to DMSO (1 mL) containing H_2O (0.1 mL, 5.6 mol), and stirring was continued for 10 min. The reaction mixture was poured into water and extracted with Et_2O. The extract was dried ($MgSO_4$) and the solvent was evaporated in vacuo. The residue was purified by chromatography (silica gel, $CHCl_3$/EtOAc, 5:1) to yield 7 mg (23 %) of **9** as an orange solid, m.p. 215−217 °C (decomp.). ^1H NMR ([D$_6$]acetone): δ = 1.81 (m, 6 H), 2.34 (m, 3 H), 2.39 (m, 6 H), 6.65 (d, *J* = 1.7 Hz, 1 H, 5-H), 7.41 (d, *J* = 1.7 Hz, 1 H, 7-H) ppm. IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1} (C=O). MS (70 eV): *m/z* (relative intensities) = 376, 378 (1:1) [M^+]. $C_{10}H_{11}BrN_4O_2$ (377.24): calcd. C 50.94, H 4.54, Br 21.18, N 14.85; found C 50.86, H 4.57, Br 21.30, N 14.75.

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