New approach to the synthesis of benzo[*e*][1,2,3,4]tetrazine 1,3-dioxides

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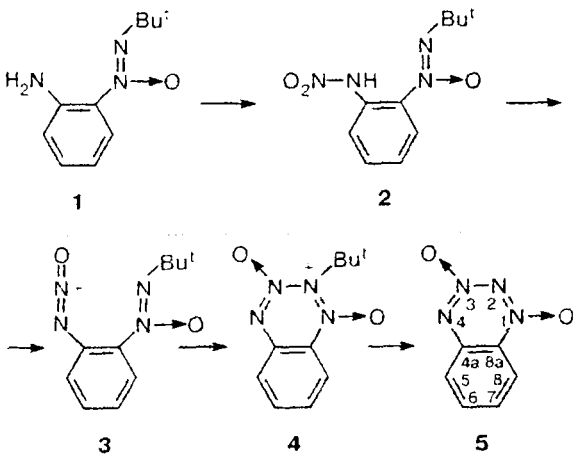
A new approach to the synthesis of benzo[*e*][1,2,3,4]tetrazine 1,3-dioxides involves the treatment of *N*-nitroanilines containing an *ortho*-(*tert*-butyl-*NNO*-azoxy) group with phosphoric anhydride or phosphorus pentachloride. The reaction is supposed to proceed through an intermediate diazonium oxide cation.

Key words: aromatic *N*-nitroamines; benzo[*e*][1,2,3,4]tetrazine 1,3-dioxides; azoxy compounds; formation of the *N*—*N* bond.

Benzo[*e*][1,2,3,4]tetrazine 1,3-dioxides (BTDO), which were synthesized for the first time at our laboratory,[1,2a] are interesting in connection with the problem of heteroaromaticity. In addition, some representatives of this class are biologically active,[3] *viz.*, they activate guanylate cyclase, a versatile controller of cell metabolism.

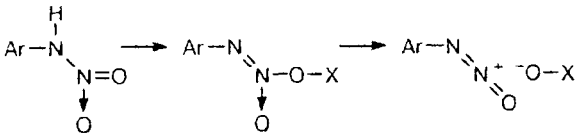
Previously,[2a] BTDO was synthesized by treating amines **1** with an excess of nitric anhydride or nitronium tetrafluoroborate. However, the use of such strong nitrating reagents leads to the formation of nitroarenes as by-products, thus revealing a drawback to this method. Supposedly, the formation of a tetrazine ring occurs when a diazonium *N*-oxide cation **3** attacks a distal nitrogen atom of an azoxy group to give intermediate **4** with subsequent elimination of the *tert*-butyl cation (Scheme 1).

Scheme 1



A possible pathway for a diazonium *N*-oxide cation* to be formed is the O-nitration of *N*-nitroamine **2** (derived from amine **1**) followed by ionic dissociation according to Scheme 2 (X—O$^-$ = NO_3^-).

Scheme 2



One can assume that the X—O$^-$ group in this scheme could be not only nitrate but also other groups capable of leaving in the form of an anion, thus generating a diazonium *N*-oxide cation. In connection with this, the goal of the present work was to search for new reagents that can transform nitramines **2** into BTDOs **5** (Scheme 1).

Cyclization was studied with 2-(*tert*-butyl-*NNO*-azoxy)-*N*-nitroaniline (**2a**) and its 4-nitro derivative (**2b**) as examples (Scheme 3). Nitramine **2a** was obtained by slow addition of a solution of N_2O_5 in MeCN to aniline **1a**. Under these conditions, the nitric acid formed during nitration binds to the starting aniline **1a**. That is why, if the reaction mixture is treated immediately after mixing the reagents, the yield of nitramine is no more than 50%; yet it can be increased to 70% by extending the reaction time. 4-Nitroaniline **1b** is less basic, and nitramine **2b** can be more conveniently obtained with the use of nitronium tetrafluoroborate at −20 °C (*cf.* Ref. 4). Mild reaction conditions minimize a possible rearrangement of *N*-nitroaniline into *C*-nitroaniline and

* For a diazonium *N*-oxide cation see Ref. 2b and the references cited therein.

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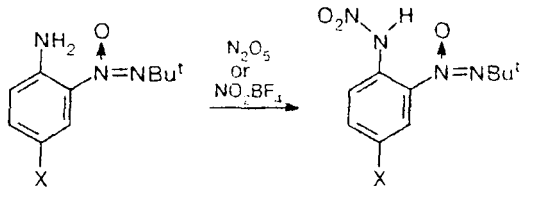
the formation of BTDOs. The structure of *N*-nitroamines **2a,b** was confirmed by ^{13}C and ^{14}N NMR spectroscopic data, which correlate well with the literature data[5] concerning this class of compounds.

Scheme 3

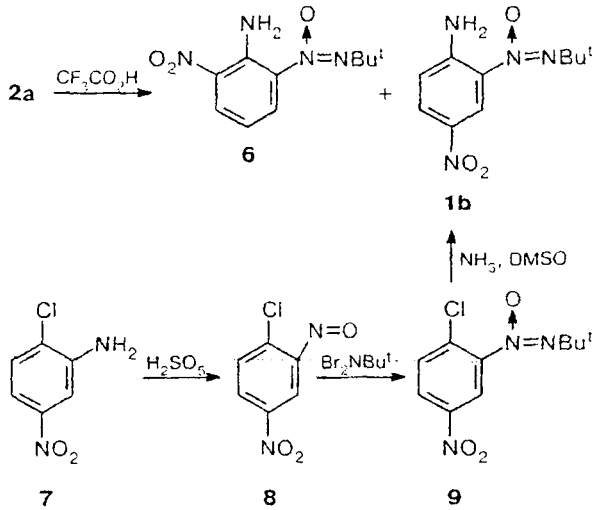


1a,b **2a,b**

X = H (**a**), NO_2 (**b**)

The synthesis of the starting aniline **1a** was described earlier.[6] Aniline **1b** was synthesized by treating with ammonia chloro derivative **9** prepared from 2-chloro-5-nitro-1-nitrosobenzene (**8**) and *N,N*-dibromo-*tert*-butylamine according to the Kovacic method[7] (Scheme 4). Nitroso compound **8** was obtained by oxidation of aniline **7** with Caro's acid. Alternatively, aniline **1b** can be formed upon rearrangement of nitramine **2a** in an acidic medium (*cf.* Ref. 4). For example, the rearrangement in trifluoroacetic acid results in *ortho*- and *para*-nitroanilines **6** and **1b** in the ratio 1 : 2.

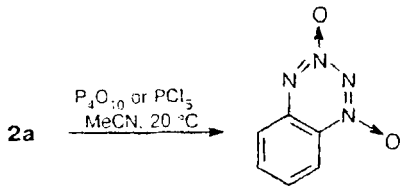
Scheme 4



It is known that reactions of nitramines with electrophiles can involve both oxygen and nitrogen atoms (see Ref. 8). At the same time, as implied by Scheme 2, only *O*-adducts can yield a diazonium *N*-oxide cation. Taking this into account, phosphorus(v) compounds were chosen as electrophiles in order to maximize the probability of an O atom being involved in the reaction.

The reaction of nitramine **2a** with phosphoric anhydride in MeCN closes a tetrazine ring to give BTDO **5a** in 63% yield (Scheme 5). The use of phosphorus pentachloride affords compound **5a** in 87% yield.

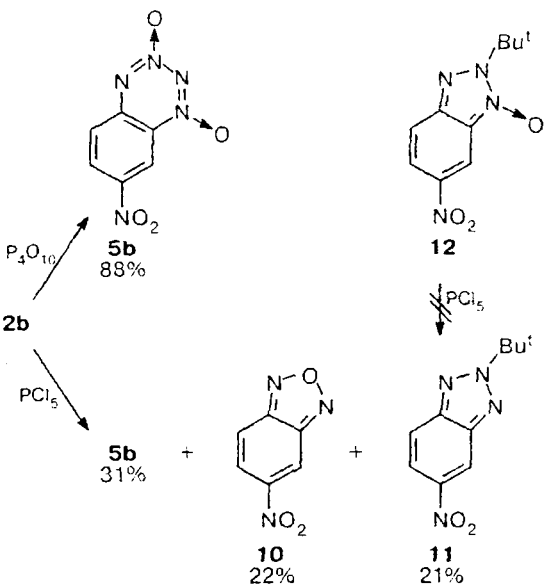
Scheme 5



5a

The presence of an electronegative nitro group in the ring strongly affects the course of the reaction. The reaction of nitramine **2b** with P_4O_{10} gave BTDO **5b** in 88% yield, while the use of PCl_5 decreases the yield of **5b** to 31% and leads to the formation of by-products **10** and **11** (Scheme 6). The structure of previously unknown benzotriazole **11** was established by using a set of physicochemical methods, including mass spectrometry (*cf.* Ref. 9) and ^1H (*cf.* Ref. 10), ^{13}C, and ^{14}N NMR spectroscopy (*cf.* Ref. 11).

Scheme 6



The mechanism of formation of benzofurazan **10** and benzotriazole **11** is still unclear. At the same time, the

formation of triazole *N*-oxide **12** would be reasonable to suppose. Indeed, when treated with PCl_5, nitramine could form an intermediate with an electrophilic nitrogen atom directly bonded to the benzene ring. Then, this electrophile could attack a distal nitrogen atom in the *tert*-butylazoxy group to give triazole *N*-oxide **12** with its possible conversion to triazole **11**. However, this sequence of transformations is invalid because an independent experiment showed that **12** decomposes under the action of PCl_5 without forming compound **11**. Note that the *tert*-butylazoxy group itself is rather stable in the presence of PCl_5. For example, compound **9** does not react with this reagent under the reaction conditions involved. Hence, it remains to assume that the *N*-oxide oxygen atom leaves the azoxy fragment in the course of an intramolecular reaction resulting in an azo-*tert*-butyl group, which further cyclizes to give triazole **11**.

Compound **5b** is resistant to PCl_5 and therefore cannot be a source of benzofurazan **10**. One of the possible pathways of formation of **10** is transformation of nitramine into a diazonium cation with subsequent intramolecular reaction involving the *tert*-butylazoxy group (*cf.* Ref. 12).

Hence, we elaborated a new approach to the synthesis of BTDO by cyclization of the corresponding *N*-nitroamines in the presence of P_4O_{10} or PCl_5. The former reagent is the most suitable for preparation of BTDOs with electronegative substituents, while the latter is preferred in the case of BTDOs without them. The method yields no nitroarenes as by-products, which makes it applicable in the cases where by-products cannot be separated by common techniques (this subject will be discussed more extensively elsewhere). In addition, the reaction under study is strong evidence in favor of the mechanism proposed for the formation of a tetrazine dioxide ring *via* an intermediate diazonium *N*-oxide cation[2b] (see Schemes 1 and 2).

Experimental

IR spectra were recorded on a Perkin—Elmer 577 spectrometer. Mass spectra were obtained with a Kratos MS-30 instrument (EI, 70 eV). ^1H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13, 75.5, 21.5, and 30.4 MHz, respectively). ^{14}N and ^{15}N chemical shifts are referred to the δ scale with nitromethane as a standard. Signals in ^{13}C NMR spectra were assigned with the use of techniques for recording spectra with selective decoupling from individual protons, selective polarization transfer from protons (SPT), two-dimensional C—H and NOE spectroscopy, and additive calculations.[13] The course of the reactions was monitored by TLC (Silufol UV-254). Silica gel was used for preparative chromatography. *N,N*-Dibromo-*tert*-butylamine[14] and 2-(*tert*-butyl-*NNO*-azoxy)aniline (**1a**)[6] were obtained according to the known procedures: N_2O_5 was prepared[15] from conc. HNO_3 and P_4O_{10} in a flow of dry argon and purified from N_2O_4 by evacuation (15 Torr, 0 °C). The procedure for the synthesis of 2-*tert*-butyl-6-nitrobenzotriazole 1-oxide (**12**) will be published elsewhere.

2-(*tert*-Butyl-*NNO*-azoxy)-*N*-nitroaniline (2a). *A.* A solution of N_2O_5 (230 mg, 2.13 mmol) in MeCN (7 mL) was cooled to −10 °C and added dropwise over 15 min to a cooled (−30 °C) solution of **1a** (400 mg, 2.07 mmol) in dry MeCN (8 mL). The reaction mixture was stirred at −20 °C for 30 min. Then, the temperature was raised to 0 °C, and CH_2Cl_2 (15 mL) was added. The resulting solution was washed with water to pH 5 and alkalized with a saturated aqueous solution of K_2CO_3 to an alkaline reaction. The unreacted starting compound **1a** was extracted with Et_2O (2 × 7 mL). An aqueous solution of the nitrammonium salt was acidified with 10% HCl, and the precipitate that formed was filtered off, washed with water, and dried *in vacuo* to give **2a** (330 mg, 67%), colorless crystals, m.p. 91—92 °C (from pentane). Found (%): C, 50.22; H, 5.88; N, 23.27. $C_{10}H_{14}N_4O_3$. Calculated (%): C, 50.41; H, 5.92; N, 23.52. IR (KBr), ν/cm^{-1}: 1495 (N(O)=N); 3115, 3180 (both bands, NH). ^1H NMR ($CDCl_3$), δ: 1.51 (s, 9 H, 3 Me); 7.32 (dt, 1 H, H(4)); 7.58 (dt, 1 H, H(5)); 7.99 (dd, 1 H, H(6), ^3J = 8.2 Hz, ^4J = 1.3 Hz); 8.08 (dd, 1 H, H(3), ^3J = 8.3 Hz, ^4J = 1.5 Hz); 12.9 (br.s, 1 H, NH). A NOE upon irradiation of the NH proton is observed on the H(6) signal, while irradiation of the *tert*-butyl group results in NOE on the H(3) signal. ^{13}C NMR ($CDCl_3$), δ: 25.7 (Me); 60.5 (C$_q$Me$_3$); 124.4 (C(3)); 125.2 (C(6)); 126.7 (C(4)); 129.6 (C(1)); 131.8 (C(5)); 137.8 (br, C(2)). Assignment was performed with consideration for the chemical shifts of 2-(*tert*-butyl-*NNO*-azoxy)aniline (**1a**).[6] ^{14}N NMR ($CDCl_3$), δ: −53 (N(O), $\Delta\nu_{1/2}$ = 60 Hz); −36 (NO_2, $\Delta\nu_{1/2}$ = 15 Hz). ^{15}N NMR INEPT ($CDCl_3$), δ: −9.9 (NBu^t). MS, *m/z*: 238 $[M]^+$.

B. NO_2BF_4 (0.5 g, 3.8 mmol) was added with stirring at −20 °C to a solution of aniline **1a** (400 mg, 2.07 mmol) in dry MeCN (5 mL). Stirring was continued at this temperature for 20 min until the starting compound disappeared (monitoring by TLC with $CHCl_3$ as eluent). Then, without raising the temperature, the reaction mixture was poured into cold water (50 mL), and products were extracted with EtOAc (3 × 15 mL). The extract was washed with a 10% aqueous solution of K_2CO_3 (2 × 20 mL) and acidified with 10% HCl to pH 4. The precipitate that formed was filtered off, washed with water, and dried *in vacuo* to give **2a** (240 mg, 49%), m.p. 91—92 °C (from pentane). The product is identical with that of method *A*.

Rearrangement of nitramine 2a. A solution of nitramine **2a** (300 mg, 1.26 mmol) in CH_2Cl_2 (1 mL) was added dropwise with stirring at 20 °C for 5 min to TFA (5 mL). Then, the reaction mixture was concentrated to dryness *in vacuo*, and the residue was washed with an aqueous solution of $NaHCO_3$ and water. The reaction products were separated by preparative TLC (silica gel, $CHCl_3$). The yield of **1b** was 135 mg (45%). The upper fraction containing nitroaniline **6** was additionally purified by chromatography (silica gel, hexane—AcOEt (7 : 1) as eluent) to give **6** (65 mg, 22%).

2-(*tert*-Butyl-*NNO*-azoxy)-4-nitroaniline (1b). Light yellow crystals, m.p. 173—174 °C (from MeOH—H_2O). Found (%): C, 50.31; H, 5.94; N, 23.37. $C_{10}H_{14}N_4O_3$. Calculated (%): C, 50.41; H, 5.92; N, 23.52. IR (KBr pellets), ν/cm^{-1}: 1340, 1500 (both bands, NO_2); 3295, 3430 (both bands, NH_2). ^1H NMR (acetone-d_6), δ: 1.49 (s, 9 H, 3 Me); 7.22 (d, 1 H, H(6), J = 8.8 Hz); 7.7 (s, 2 H, N—H); 8.08 (dd, 1 H, H(5)); 8.90 (d, 1 H, H(3), J = 2.2 Hz). ^{13}C NMR (DMSO-d_6), δ: 25.0 (CH_3); 58.5 (C$_q$Me$_3$); 117.1 (C(6), $^3J_{NH_2}$ = 8.2 Hz); 121.0 (C(3), ^3J = 5 Hz); 125.9 (C(5), J = 6 Hz); 128.8 (br, C(2)); 134.6 (C(4), ^3J = 11 Hz, ^2J = 4 Hz); 147.6 (C(1), $^3J_{H(3)}$ = 5 Hz, $^3J_{H(5)}$ = 9 Hz). ^{14}N NMR (acetone-d_6), δ: −51 (N(O), $\Delta\nu_{1/2}$ = 30 Hz); −13 (NO_2, $\Delta\nu_{1/2}$ = 70 Hz). ^{15}N NMR (DMSO-d_6), δ: −191.6 (NH_2); −50.8 (N(O)); −17.0 (NBu^t); −12.8 (NO_2). MS, *m/z*: 238 $[M]^+$.

2-(*tert*-Butyl-*NNO*-azoxy)-6-nitroaniline (6). Bright yellow crystals, m.p. 74—75 °C (from EtOH—H_2O). Found (%): C, 50.38; H, 5.90; N, 23.36. $C_{10}H_{14}N_4O_3$. Calculated (%): C, 50.41; H, 5.92; N, 23.52. IR (KBr pellets), ν/cm^{-1}: 1360, 1520 (both bands, NO_2); 3300, 3425 (both bands, NH_2). ^1H NMR (DMSO-d_6), δ: 1.46 (s, 9 H, 3 Me); 6.79 (t, 1 H, H(4), ^3J = 8.0 Hz); 7.8 (s, 2 H, N—H); 8.12 (dd, 1 H, H(5), ^3J = 8.0 Hz, ^4J = 1.6 Hz); 8.26 (dd, 1 H, H(3), ^3J = 8.0 Hz, ^4J = 1.6 Hz). Irradiation of the *tert*-butyl protons results in NOE on the H(3) signal. ^{13}C NMR (DMSO-d_6), δ: 25.4 (CH_3); 59.4 ($\underline{C}Me_3$); 113.8 (C(4)); 129.1 (C(3)); 131.5 (C(5)); 133.6 br, 136.0 br (C(2) and C(6)); 139.0 (C(1)). ^{14}N NMR ($CDCl_3$), δ: −51 (N(O), $\Delta\nu_{1/2}$ = 35 Hz); −11 (NO_2, $\Delta\nu_{1/2}$ = 70 Hz). MS, *m/z*: 238 $[M]^+$.

2-(*tert*-Butyl-*NNO*-azoxy)-4-nitroaniline (1b) from compound 9. Gaseous NH_3 was passed through a solution of compound **9** (5 g, 19.4 mmol) in 60 mL of dry DMSO at 100 °C for ~8 h until **9** had disappeared completely (monitoring by TLC with $CHCl_3$ as eluent). The reaction mixture was cooled to ~20 °C and poured into 200 mL of water. The precipitate that formed was filtered off and washed with water. Recrystallization from an aqueous solution of MeOH gave aniline **7** (3.7 g, 80%), m.p. 173—174 °C. The product is identical with that described above.

2-(*tert*-Butyl-*NNO*-azoxy)-*N*,4-dinitroaniline (2b). NO_2BF_4 (600 mg, 4.5 mmol) was added with stirring to a solution of aniline **1b** (500 mg, 2.1 mmol) in dry MeCN (10 mL) at −20 °C. Stirring was continued at this temperature for 20 min until the starting compound disappeared (monitoring by TLC with benzene as eluent). Without raising the temperature, the reaction mixture was poured into cold water (100 mL). The precipitate that formed was filtered off and dried in air. Recrystallization from hexane gave aniline **2b** (360 mg, 61%), m.p. 94—96 °C. Found (%): C, 42.56; H, 4.68; N, 24.51. $C_{10}H_{13}N_5O_5$. Calculated (%): C, 42.40; H, 4.63; N, 24.73. IR (KBr pellets), ν/cm^{-1}: 1350, 1530 (both bands, NO_2); 1500 (N(O)=N); 3110, 3150 (both bands, NH). ^1H NMR (DMSO-d_6), δ: 1.39 (s, 9 H, 3 Me); 7.69 (d, 1 H, H(6)); 8.46 (dd, 1 H, H(5), ^3J = 8.8 Hz, ^4J = 2.6 Hz); 8.58 (d, 1 H, H(3)). ^1H NMR ($CDCl_3$), δ: 1.55 (s, 9 H, 3 Me); 8.44 (m, 2 H, H(5) and H(6)); 9.07 (s, 1 H, H(3)); 13.80 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 25.2 (CH_3); 59.5 ($\underline{C}Me_3$); 120.4 (C(3)); 125.9 (C(5)); 128.0 (C(6)); 132.7 (C(1)); 143.3 (br, C(2)); 146.2 (C(4)). ^{14}N NMR ($CDCl_3$), δ: −56 (N(O), $\Delta\nu_{1/2}$ = 85 Hz); −41 (N—$\underline{N}O_2$, $\Delta\nu_{1/2}$ = 40 Hz); −18 (NO_2, $\Delta\nu_{1/2}$ = 200 Hz). MS, *m/z*: 283 $[M]^+$.

1-Chloro-4-nitro-2-nitrosobenzene (8). A solution of Caro's acid was prepared as follows.[16] A mixture of ammonium persulfate (38 g) and conc. H_2SO_4 (25 mL) was stirred at 20 °C for 1 h and poured into ice (180 g). Finely ground 2-chloro-5-nitroaniline (**7**) (3 g, 17.4 mmol) was stirred at 20 °C for 1 h with 5 mL of conc. H_2SO_4 and 10 mL of water. The resulting suspension was added to a solution of Caro's acid and stirred at 0 °C for 5 h. The precipitate that formed was filtered off, washed with conc. HCl in order to remove the unreacted starting aniline **7** and with water, and dried *in vacuo* over P_4O_{10} to give nitroso compound **8** (3.1 g, 95%), m.p. 118—120 °C (from EtOH) (see Ref. 17). Found (%): C, 38.81; H, 1.63; N, 14.92. $C_6H_3ClN_2O_3$. Calculated (%): C, 38.63; H, 1.62; N, 15.02. IR (KBr pellets), ν/cm^{-1}: 1350, 1530 (NO_2). ^1H NMR ($CDCl_3$), δ: 7.04 (d, 1 H, H(3), ^4J = 2.7 Hz); 8.03 (d, 1 H, H(6), ^3J = 8.6 Hz); 8.51 (dd, 1 H, H(5)). MS, *m/z*: 186 $[M]^+$.

2-(*tert*-Butyl-*NNO*-azoxy)-1-chloro-4-nitrobenzene (9). A solution of *N*,*N*-dibromo-*tert*-butylamine (2.9 g, 12.6 mmol) in 20 mL of CH_2Cl_2 was added with stirring at 0 °C to a solution of nitroso compound **8** (2.3 g, 12.4 mmol) in 30 mL of CH_2Cl_2 and 30 mL of MeCN. The reaction mixture was kept at 20 °C for 4 h and then concentrated *in vacuo*. Recrystallization from an aqueous solution of MeOH gave compound **9** (2.4 g, 75%), m.p. 106—108 °C. Found (%): C, 46.65; H, 4.70; Cl, 13.70; N, 16.19. $C_6H_3ClN_2O_3$. Calculated (%): C, 46.61; H, 4.69; Cl, 13.76; N, 16.31. IR (KBr pellets), ν/cm^{-1}: 1355, 1535 (NO_2); 1495 (N(O)=N). ^1H NMR (acetone-d_6), δ: 1.49 (s, 9 H, 3 Me); 7.91 (d, 1 H, H(6), ^3J = 8.8 Hz); 8.37 (dd, 1 H, H(5)); 8.47 (d, 1 H, H(3), ^4J = 2.6 Hz). ^{13}C NMR (acetone-d_6), δ: 25.7 (CH_3); 61.0 ($\underline{C}Me_3$); 120.8 (C(3)); 126.0 (C(5), ^3J = 5.2 Hz); 133.0 (C(6)); 133.4 (C(1), $^3J_{H(3)}$ = 7.8 Hz); 147.9 (slightly br.s, C(4), ^3J = 9.6 Hz); 148.4 (br.s, C(2)). ^{14}N NMR (acetone-d_6), δ: −50 (N(O), $\Delta\nu_{1/2}$ = 50 Hz); −11 (NO_2, $\Delta\nu_{1/2}$ = 80 Hz). MS, *m/z*: 257, 259 (1 : 0.3) $[M]^+$.

Reaction of nitramine 2a with P_4O_{10}. Phosphoric anhydride (3 g) was added to a solution of nitramine **2a** (300 mg, 1.3 mmol) in dry MeCN (20 mL). The reaction mixture was stirred for 15 min until the starting compound disappeared (monitoring by TLC with $CHCl_3$ as eluent) and then poured into cold water (200 mL). The products were extracted with EtOAc and dried with $MgSO_4$, and the solvent was removed *in vacuo*. The residue was purified by chromatography ($CHCl_3$ as eluent) to give benzo[*e*][1,2,3,4]tetrazine 1,3-dioxide (**5a**) (130 mg, 63%), m.p. 170—172 °C. The product is identical with an authentic sample.[2a]

Reaction of nitramine 2a with PCl_5. Phosphorus pentachloride (0.8 g) was added to a solution of nitramine **2a** (200 mg, 0.8 mmol) in dry MeCN (15 mL). The reaction mixture was stirred for 15 min until the starting compound disappeared (monitoring by TLC with $CHCl_3$ as eluent) and then treated as described above to give **5a** (120 mg, 87%).

Reaction of nitramine 2b with P_4O_{10}. Phosphoric anhydride (1.7 g) was added to a solution of nitramine **2b** (200 mg, 0.71 mmol) in dry MeCN (15 mL). The reaction mixture was stirred for 40 min until the starting compound disappeared (monitoring by TLC with benzene as eluent) and then poured into cold water (150 mL). The products were extracted with EtOAc and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the residue was washed with hexane to give 7-nitrobenzo[*e*][1,2,3,4]tetrazine 1,3-dioxide (**5b**) (130 mg, 88%), m.p. 166—168 °C. The product is identical with an authentic sample.[2a]

Reaction of nitramine 2b with PCl_5. Phosphorus pentachloride (0.8 g) was added to a solution of nitramine **2b** (200 mg, 0.7 mmol) in dry MeCN (4 mL). The reaction mixture was stirred for 10 min until the starting compound disappeared (monitoring by TLC with benzene as eluent) and then poured into cold water (50 mL). The products were extracted with EtOAc and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the residue was separated by chromatography (benzene as eluent) to give **5b** (46 mg, 31%), **11** (34 mg, 22%), and 5-nitrobenzofurazan (**10**) (25 mg, 21%), m.p. 63—65 °C (from hexane) (*cf.* Ref. 18: m.p. 64—65 °C). The product is identical with an authentic sample.[18]

2-*tert*-Butyl-5-nitrobenzotriazole (11). Colorless crystals, m.p. 110—111 °C. Found (%): C, 54.27; H, 5.31; N, 25.81. $C_{10}H_{12}N_4O_2$. Calculated (%): C, 54.54; H, 5.49; N, 25.44. IR (KBr pellets), ν/cm^{-1}: 1350, 1530 (both bands, NO_2). ^1H NMR (acetone-d_6), δ: 1.86 (s, 9 H, 3 Me); 8.11 (d, 1 H, H(7)); 8.23 (dd, 1 H, H(6), ^3J = 8.8 Hz, ^4J = 2.3 Hz); 8.87 (d, 1 H, H(4)). ^{13}C NMR (acetone-d_6), δ: 29.9 (CH_3); 67.3 ($\underline{C}Me_3$); 116.8 (C(4)); 120.3 (C(7), $^4J_{H(4)}$ = 1.5 Hz); 121.0 (C(6), $^3J_{H(4)}$ = 4.8 Hz); 143.2 (C(3a), $^2J_{H(4)}$ = 1.6 Hz, $^3J_{H(7)}$ = 5.7 Hz); 146.9 (C(7a), $^3J_{H(4)}$ = 5.4 Hz); 147.2 (br, C(5)). ^{14}N NMR (acetone-d_6), δ: −78 (NBu^t, $\Delta\nu_{1/2}$ = 120 Hz); −12 (NO_2, $\Delta\nu_{1/2}$ = 110 Hz). MS, *m/z*: 220 $[M]^+$.

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