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# Synthesis of [1,2,5]Oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-Di-*N*-oxide

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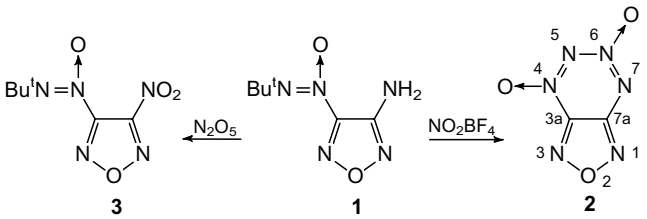
Treatment of 3-amino-4-(*tert*-butyl)azoxyfurazan with $NO_2BF_4$ in MeCN gives [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-di-*N*-oxide **2**; $^{15}N$ labelling experiments allowed the spectra of **2** to be fully assigned and provided support for the proposed structure. Diazonium oxide cation is proposed as the intermediate in ring closure.

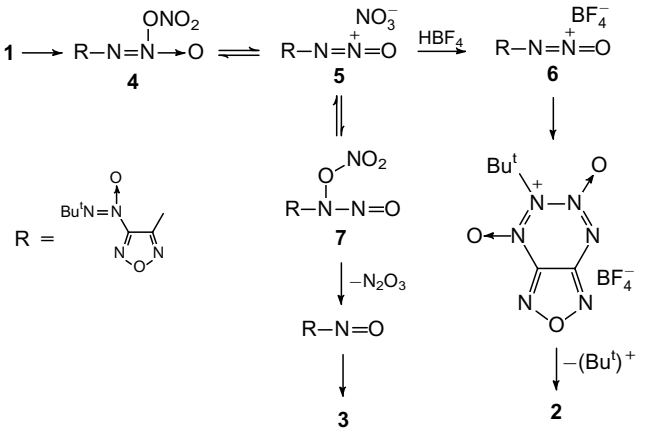
It was disclosed recently[1] that dinitrogen pentaoxide was an effective reagent for cyclisation of *o*-(*tert*-butyl-*NNO*-azoxy)-anilines into benzo-1,2,3,4-tetrazine 1,3-di-*N*-oxides. Nevertheless, this reagent did not convert 3-amino-4-*tert*-butylazoxyfurazan **1** to [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-di-*N*-oxide **2**. Instead, oxidation of the amino group took place[2] to produce the nitro compound **3**.

In the present communication the synthesis of **2** is



**Scheme 1**

described. This compound was obtained when amine **1** was treated with excess nitronium tetrafluoroborate.† To explain such a great difference between $N_2O_5$ and $NO_2BF_4$, we suggest the following reaction mechanism. The treatment of amine **1** with nitrating reagents, both $N_2O_5$ and $NO_2BF_4$, results in intermediate **4**, which is in equilibrium with ionic pair **5**. In the case of $N_2O_5$, cyclisation does not occur and the diazonium oxide cation reacts with $NO_3^-$ anion to give **7**, which is a precursor of nitro compound **3** (see ref. 2). In the case of $NO_2BF_4$, the exchange of ligands results in the ionic pair **6** which is electrophilic enough to react with the *tert*-butylazoxy group to produce bicycle **2**. The proposed mechanism is a good argument in favour of the fact that cation $-N{=}N{=}O^+$ exists as an intermediate in ring closure (Scheme 2).

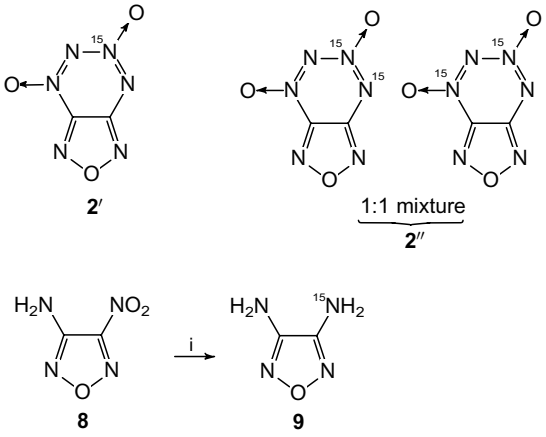


**Scheme 2**

Bicycle **2** is the first known compound in which the 1,2,3,4-tetrazine 1,3-di-*N*-oxide ring is fused with a five-membered ring. It gives bright yellow crystals (m.p. 110–112 °C, decomp.) which can be stored at 0 °C for a long time. It is not as stable as benzo-1,2,3,4-tetrazine 1,3-dioxides,[1] but more stable than the very similar 2-phenyl-2*H*-[1,2,3]triazolo-[4,5-*e*][1,2,3,4]tetrazine,[3] which does not have *N*-oxide oxygen atoms.

The structure of **2** was confirmed by $^{13}C$ NMR (two C atoms were observed), $^{17}O$ NMR (three O atoms were observed) and $^{14}N$ NMR, where two narrow signals of N(4) and N(6) atoms were observed.‡ The latter were located in the same interval as the signals of N(1) and N(3) atoms of benzo-1,2,3,4-tetrazine 1,3-di-*N*-oxides.[1] To obtain unambiguous proof of the structure, $^{15}N$ NMR investigations were accomplished. Labelled compound **2′** was obtained according to Scheme 1 using labelled $^{15}NO_2BF_4$ (enrichment factor 96%).

The reaction of aminonitrofurazan[5] **8** with labelled $^{15}NH_3$ under high pressure§ gave diaminofurazan **9** labelled on one amino group (Scheme 3). This was a starting material for labelled 3-amino-4-(*tert*-butyl)azoxyfurazan,[2] which after reaction with $^{15}NO_2BF_4$ gave compound **2″** in which the $^{15}N$ enrichment factor for N(6) atom is 96%, while for N(4) and N(7) atoms it is 48%. The $^{15}N$ NMR investigations of **2** based on natural isotope content and investigations of labelled **2′** and **2″** allowed one to assign all nitrogen signals of the tetrazine dioxide ring, to ascertain the relative positions of N atoms and thus to establish the arrangement of the *N*-oxide oxygen atoms.



**Scheme 3** *Reagents and conditions*: i, $^{15}NH_3$ (enrichment factor 96%), MeCN, autoclave, 14 kbar, 5 h, 80 °C (degree of conversion 69%, yield 91% with respect to the converted **8**).

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† A procedure for the synthesis of **2** is as follows: **Caution!** This compound is very sensitive to shock and should be handled with care. To a stirred and cooled (−20 °C) solution of **1** (1 g, 5.4 mmol) in dry MeCN (50 ml) was added $NO_2BF_4$ (3 g, 22.6 mmol). After being gradually warmed to room temperature, the mixture was stirred for 4 h and the solvent was removed *in vacuo*. $CH_2Cl_2$ (100 ml) was added, the solution was washed with ice-cold water (20 ml) and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 50 ml). The combined $CH_2Cl_2$ solution was dried ($MgSO_4$), concentrated *in vacuo* and filtered through silica gel (10 g). The solvent was removed *in vacuo* to give a yellow solid, m.p. 95–103 °C (decomp.), which was purified by chromatography (silica gel, $CHCl_3$) to yield 0.44 g (52%) of **2** as bright yellow crystals, m.p. 110–112 °C (decomp).

‡ *Spectroscopic data for* **2**: IR[4] (KBr) 1520, 1570; $^{13}C$ NMR ([$^2H_6$]acetone/$CD_2Cl_2$) δ 143.5 (br, C-3a), 155.75 (C-7a); $^{14}N$ NMR ([$^2H_6$]acetone/$CD_2Cl_2$, $MeNO_2$ as the standard) δ −44 ($\nu_{1/2}$ = 100 Hz) (N-6), −53 ($\nu_{1/2}$ = 15 Hz) (N-4), −105 ($\nu_{1/2}$ = 500 Hz) (N-7); $^{15}N$ NMR ([$^2H_6$]acetone/$CD_2Cl_2$, $MeNO_2$ as the standard) δ 35.0, 38.2 (N-1 and N-3), 8.0 (br, N-5), −43.9 (N-6), −52.8 (N-4), −106.0 (N-7); $^{17}O$ NMR ([$^2H_6$]acetone/$CD_2Cl_2$ 1:1) δ 452 ($\nu_{1/2}$ = 800 Hz); 508 ($\nu_{1/2}$ = 500 Hz); 542 ($\nu_{1/2}$ = 600 Hz) (integral intensity 1:1:1); MS, *m/z* (EI) 156 (20, $M^+$), 84 (8, $M^+ - N_2 - N_2O$), 68 (56, $M^+ - 2N_2O$), 52 (100). Found: C 15.61; N 53.55%. Calc. for $C_2N_6O_3$: C 15.39; N 53.85%.

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