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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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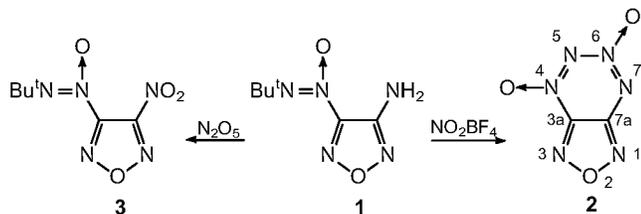
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Treatment of 3-amino-4-(*tert*-butyl)azoxyfuran with  $\text{NO}_2\text{BF}_4$  in MeCN gives [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-di-*N*-oxide **2**;  $^{15}\text{N}$  labelling experiments allowed the spectra of **2** to be fully assigned and provided support for the proposed structure. Diazonium oxide cation is proposed as the intermediate in ring closure.

It was disclosed recently<sup>1</sup> 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*-butylazoxy-

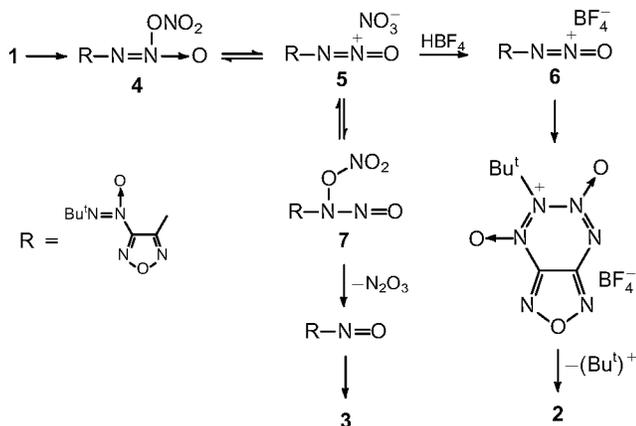
furan **1** to [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine 4,6-di-*N*-oxide **2**. Instead, oxidation of the amino group took place<sup>2</sup> to produce the nitro compound **3**.

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.<sup>†</sup> 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,<sup>1</sup> but more stable than the very similar 2-phenyl-2*H*-[1,2,3]triazolo-[4,5-*e*][1,2,3,4]tetrazine,<sup>3</sup> which does not have *N*-oxide oxygen atoms.

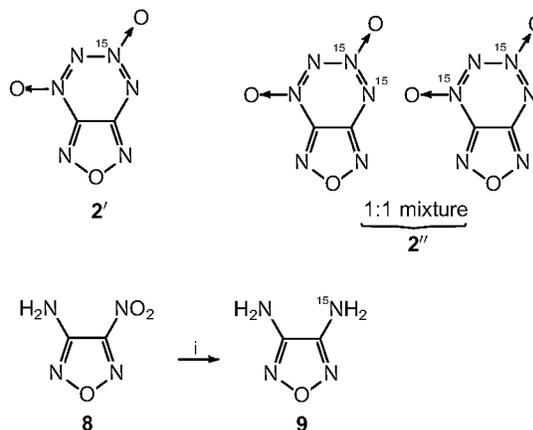
The structure of **2** was confirmed by  $^{13}C$  NMR (two C atoms were observed),  $^{17}O$  NMR (three O atoms were observed) and  $^{14}N$  NMR, where two narrow signals of N(4) and N(6) atoms were observed.<sup>‡</sup> The latter were located in the

<sup>†</sup> 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.).

<sup>‡</sup> Spectroscopic data for **2**: IR<sup>4</sup> (KBr) 1520, 1570;  $^{13}C$  NMR ( $[^2H_6]$ acetone/ $CD_2Cl_2$ )  $\delta$  143.5 (br, C-3a), 155.75 (C-7a);  $^{14}N$  NMR

same interval as the signals of N(1) and N(3) atoms of benzo-1,2,3,4-tetrazine 1,3-di-*N*-oxides.<sup>1</sup> To obtain unambiguous proof of the structure,  $^{15}N$  NMR investigations were accomplished. Labeled compound **2'** was obtained according to Scheme 1 using labelled  $^{15}NO_2BF_4$  (enrichment factor 96%).

The reaction of aminonitrofurazan **8** with labelled  $^{15}NH_3$  under high pressure<sup>§</sup> gave diaminofurazan **9** labelled on one amino group (Scheme 3). This was a starting material for labelled 3-amino-4-(*tert*-butyl)azoxyfuran,<sup>2</sup> 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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( $[^2H_6]$ acetone/ $CD_2Cl_2$ , MeNO<sub>2</sub> as the standard)  $\delta$  –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<sub>2</sub> as the standard)  $\delta$  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)  $\delta$  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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