Unusual oxidation of 4-amino-4H,8H-bisfurazano[3,4-b:3',4'-e]pyrazines

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The oxidation of 4,8-diamino-4*H*,8*H*-bisfurazano[3,4-b:3',4'-e]pyrazine 1 with positive halogen reagents and related oxidants afforded a stable nitrogen-centered radical, bisfurazano[3,4-b:3',4'-e]pyrazine biradical 4; tetrazene 2 was a probable intermediate.

Previously, high-nitrogen furazan derivatives that are attractive ingredients for gas-generating pyrotechnic compositions were described.¹⁻³

We recently reported the synthesis of a new high-nitrogen macrocycle incorporating the 4H,8H-bisfurazano[3,4-b:3',4'-e]-pyrazine moiety by the oxidative cyclization of a linear precursor with terminal amino groups at a furazan ring using dibromo-isocyanurate.⁴ To extend the study, we investigated the similar oxidation of an *N*-aminopiperazine, *viz.*, 4,8-diamino-4H,8H-bisfurazano[3,4-b:3',4'-e]pyrazine **1**.⁵

The oxidation of N-aminoheterocycles by *tert*-butyl hypochlorite, (diacetoxyiodo)benzene, or lead tetraacetate (LTA) usually leads to the formation of three types of products: (i) a *trans*tetrazene, (ii) a new heterocycle from the ring expansion of the starting heterocycle by N-nitrene intermediate rearrangement, and (iii) the parent NH-heterocycle.^{6–8} The methods of synthesis and the chemistry of N-aminoheterocycles were reviewed previously.⁹

When N-amine 1 was treated with an excess of dibromoisocyanurate in MeCN at room temperature, the product was neither desired tetrazene 2 nor tetrazocine 3^{10} (Scheme 1). The structure of the dark violet product was identified as the biradical 4^{\dagger} by comparison with the mp and spectral data for an authentic sample.^{5,11,12} Other oxidants {*tert*-butyl hypochlorite, (diacetoxyiodo)benzene, [bis(trifluoroacetoxy)iodo]benzene (BTI), perchloryl fluoride, xenon difluoride, and LTA} also reacted with N-amine 1 in a similar fashion. This type of reactions has not been observed previously in other N-aminoheterocycles.¹³



Scheme 1 Reagents and conditions: i, dibromoisocyanurate, MeCN, 20 °C, 5 min, 94%.

A probable mechanism involving initial tetrazene intermediate formation (*e.g.*, of type **2**) followed by the loss of nitrogen and the generation of biradical **4** can be suggested. In fact, it was found that the oxidation of N,N'-diamine **1** with LTA in CH₂Cl₂/CF₃CO₂H at -40 to -30 °C did not lead to the loss of nitrogen, and an extremely explosive solid, probably tetrazane **2**,[‡] was formed. The solid gave biradical **4** with the loss of nitrogen on heating to room temperature.

The oxidation of the monoamine 5^5 by treatment with dibromoisocyanurate led to the same biradical 4. An initial tetrazene



Scheme 2 Reagents and conditions: i, dibromoisocyanurate, MeCN/CH₂Cl₂, 20 °C, 56%; ii, Bu'OCl, CF₃CO₂H/CHCl₃, -5-0 °C, 38%; iii, PrⁱOH/Δ.

was evidently intermediate in this case. The result of reaction of amine **5** with *tert*-butyl hypochlorite in acidic conditions confirmed this assumption (Scheme 2). The mixture produced a dark coloured solution, presumably due to the formation of a radical. Proton rich conditions favoured hydrogen abstraction from the solvent by the radical. The dark violet colour was substantially discharged rapidly upon heating to room temperature. The resulting brown solid was purified by flash column chromatography (SiO₂; PrⁱOH–diethyl ether, 7:1) to afford tetrazene **6**.[§] Compound **6** is an extremely labile yellow solid, which can explode when heated or scratched. On recrystallization from isopropanol, it was converted into dihydro compound **7**.^{11,14}

We prepared other mono-*N*-aminopiperazines **8a–c** by the N-amination of monosubstituted 4H,8*H*-bisfurazano[3,4-*b*:3',4'-*e*]-pyrazines **7a–c**¹² with hydroxylamine-*O*-sulfonic acid according to the published procedure⁵ (Scheme 3). When amines **8a** and **8b** were subjected to the same oxidation conditions as in Scheme 2, the corresponding tetrazenes were not detected in the reaction mixture; the mixture was observed to turn dark

Selected data for **6**: mp 159–164 °C (explosion!). ¹H NMR ([²H₆]DMSO) δ : 11.8 (NH). ¹³C NMR ([²H₆]DMSO) δ : 145.0 (C–NH), 152.8 (C–NN=N). MS (EI), *m/z*: 358 (M⁺), 330 (M⁺ – N₂), 328 (M⁺ – N₂ – H₂), 300 (M⁺ – N₂ – NO). Calc. for C₈H₂N₁₄O₄: 358.20. IR, *v*/cm⁻¹: 3240–3260, 1640, 1580, 1110, 985, 860.

For **8a**: mp 210–213 °C. ¹H NMR ([²H₆]DMSO) δ: 3.41 (3H, Me), 5.7 (2H, NH₂). For **8b**: mp 171–174 °C (decomp.). ¹H NMR ([²H₆]DMSO) δ: 6.7 (NH₂). MS (EI), *m/z*: 303 (M⁺). For **8c**: mp 208–210 °C (decomp.). ¹H NMR ([²H₆]DMSO) δ: 6.3 (NH₂), 8.9 (CH). MS (EI) *m/z*: 285 (M⁺).

^{\dagger} Biradical **4** was found to be stable as a solid in storage at room temperature (more than 3 years). It is soluble in common organic solvents; however, it rapidly decomposed in solution (as the result of hydrogen abstraction from the solvent). Biradical **4** is an explosive of moderate sensitivity and should be handled with care.

^{*} **Warning!** It is a dangerous primary explosive. In a solid form at -70 °C it was subject to spontaneous explosion.

[§] Compounds described in this communication are explosives and should be handled with appropriate precautions. All new compounds gave satisfactory spectroscopic and analytical results.

For **9**: the compound exploded when tested for melting point. IR (KBr, ν/cm^{-1}): 1640, 1597, 1575, 1430, 1350, 1305, 1190, 1150, 1085, 965. Found (%): C, 22.46; N, 41.74. Calc. for C₅N₈O₆ (268.11) (%): C, 22.40; N, 41.79.

blue in 10 min, but no detectable product was formed. Similar results were obtained with (diacetoxyiodo)benzene, BTI, and $Na_2S_2O_8$ -CF₃CO₂H as oxidants. On the other hand, the oxidation of amine **8c** with $Na_2S_2O_8$ -CF₃CO₂H gave an unusual poorly soluble light yellow product that precipitated from the reaction mixture (Scheme 3).



Scheme 3 Reagents and conditions: i, $Na_2CO_3-H_2NOSO_3H-H_2O$ -dioxane, 60–75 °C, 37–62%; ii, $Na_2S_2O_8-CF_3CO_2H$ -glyme, room temperature, 24%.

The light yellow solid darkened on heating above 75 °C. At about 110 °C, it decomposed with the release of nitrogen oxides. IR spectra of the solid show the presence of the nitro group at 1350 and 1575 cm⁻¹. The ¹H NMR spectrum ([²H₆]DMSO) confirmed the absence of any hydrogen atoms in the compound, but low solubility prevented the collection of ¹³C NMR data. The ¹⁴N NMR spectrum is comparable with that of starting compound 7c (a singlet). However, the ¹⁴N NMR spectrum of the compound shows a downfield resonance at -42.1 ppm (NO₂) as compared to -35.6 ppm for the same nitrogen atom in 7c. This observation can be accounted for only if the hydrogen atom at the dinitromethyl group was replaced by an electronwithdrawing substituent as in oligomer 9.8 Microanalysis gave the molecular formula $C_5N_8O_6$, indicating the same structure of 9. Mass spectrometric analysis was impossible due to the instability of compound 9 under the ionization conditions; only small fragments were observed in the spectrum.

In conclusion, the difference in behaviour of these N-amino compounds clearly shows the importance of a substituent at the second piperazine nitrogen atom. The oxidation of 4,8-diamino-4H,8H-bisfurazano[3,4-b:3',4'-e]pyrazine represents the first example of formation of a stable aminyl radical by the oxidative deamination of an N-amino heterocycle.

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