Synthesis and Characterization of Bisnitrofurazanodioxadiazine (BNFOZ)

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Nitro and amino 1,2,5-oxadiazoles (furazans) have been considered as explosives and propellants, because they have high nitrogen content, good oxygen balance, and high energy density.[1] A 1,2,5-oxadiazole-2-oxide (furoxan) is also a highly energetic heterocycle, and replacement of a furazan to a furoxan is a method to increase crystal density and improve explosive performance.[2] In addition, furoxans have biological activities related to nitrogen oxide.[3] Furazan rings were readily prepared from glyoxal and other reagents,[2,4] but direct oxidation of furazan to furoxan has not been reported yet. 3,4-Dintrofurazan and 3,4-dinitrofuroxan have a positive oxygen balance and powerful performance, but they exhibit poor thermal stability and impact sensitivity as practical explosives.[2]

Among the high energy materials, as furoxan derivatives, one of the most promising molecular explosives was 7-amino-4,6-dinitrobenzofuroxan (ADNBF), which is more impact insensitive and has good explosive properties.[2] And also 3,4-bis(nitrofurazano)furoxan (BNFF, **5**), consisted of nitrofurazan and furoxan, was a well known compound as a novel energetic material. It has high density (1.937 g/cm³), and exhibits high detonation velocity (~9250 m/s) and detonation pressure (~45.8 Gpa), comparable to HMX.[5]

BNFF could be prepared from malononitrile by multistep process, including the Sandmeyer reaction, dimerization of a nitrile oxide, followed by oxidation.[6] Other synthetic method was not practical, because *n*-BuLi and TMSCl were employed, and the yield was rather low.[7] When chloroxime **1**, a key intermediate, prepared from malononitrile was treated with base, dimerization reactions took place to afford ring compounds, without the isolation of intermediate nitrile oxide **2**. In the previous reports, the dimerization of nitrile

oxide **2** gave a mixture of BAFF (**3**) and 3,6-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,4,2,5,-dioxadiazine (BAFOZ, **4**) under the almost same reaction condition (Scheme **1**).[6,8]

Most of the high energetic molecules are comprised of a nitro group. The amino groups in BAFF were oxidized with CH₃CO₃H or H₂O₂ to give BNFF in moderate yield.[7,9] In this report, we tried to understand the dimerization reaction and find a better oxidation condition to synthesize BNFF, and 3,6-bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (BNFOZ, **4**), an isomer of BNFF.

Results and Discussion

Since a furazan was not converted to a furoxan by direct oxidation, a 1,3-dipolar cyclization of a nitrile oxide was one of the most important methods to afford a furoxan, in addition to other methods.[2] Nitrile oxides are generated from hydroximoyl halides, oximes, nitrolic acids and primary nitroalkanes. In the reaction of hydroximoyl halides, and nitrolic acids, an aqueous base or triethylamine was used to eliminate hydrogen chloride and nitrous acid. During the reaction, the corresponding nitrile oxide was not isolated and the further reaction took place to afford several products like furoxans, 1,2,4-oxadiazole-4-oxides, 1,4-dioxa-2,5-diazines, and nitrile oxide-derived polymers.[10]

In the dimerization of nitrile oxide **2**, potassium carbonate gave better result than potassium hydroxide. Counter cations of carbonate did not much affect the product mixture. When the reactions took place with higher concentration of base or at higher temperature, a portion of unknown compounds increased. When the reaction was carried out in the mixture of aqueous base with ether, ethyl acetate, or methylene chloride, BAFF was given as a major product. On the other hand, solvents like THF, acetonitrile and methanol afforded BAFOZ as a major one.[6] And BAFOZ was also major in aqueous base or using triethylamine in ether and aceto-nitrile.[11] Under these reaction conditions, the 1,2,4-oxadia-zole-4-oxide isomer was not obtained as a major compound and small amount of unknown polymeric materials was often observed.[6] Some of these results were different from other dimerizations under similar reaction conditions.[3f]

On the basis of molecular orbital calculations, the mechanism of forming 5-membered structures was proposed stepwise via diradical intermediate, instead of concerted 1,3-dipolar cyclization.[12] But the formation of 6-membered compounds has not been reported yet. By a calculation,
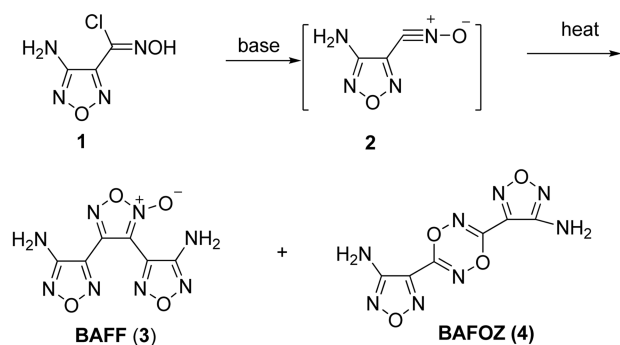
Scheme 1. A Synthesis of BAFF and BAFOZ.

1,2,4-oxadiazole-4-oxides are thermodynamically more favorable than 1,2,5-oxadiazole-2-oxides (furoxans)[12] and BAFOZ is more stable than BAFF by 10.59 kcal/mol.[13] In experiment, BAFOZ or BAFF was given as a major compound depending on the reaction conditions, but the corresponding 1,2,4-oxadiazole-4-oxide was not observed as a major compound.[6]

In the presence of a radical scavenger such as phenol and benzoquinone, the formation of BAFF or BAFOZ was not much affected, resulting that the major compound was not changed. When diphenylamine was added into the solution of chloroxime **1** in THF-aq. K_2CO_3, the mixture was separated in two layers and BAFOZ or BAFF was not given as a major compound. When THF was added until the mixture became homogeneous, BAFOZ was again major. As a result, the homogeneity was important to control the reaction path of the dimerization. BAFF was major in heterogeneous conditions as in ether-aq. K_2CO_3, while BAFOZ was in homogeneous ones as in THF-aq. K_2CO_3.[6]

The oxidation of amino groups attached to furazans gave mainly nitro as well as other functional groups, such as nitro, diazo, azoxy, and their mixture.[14] In the previous report, the oxidation of BAFF with 96% H_2O_2 and TFAA gave BNFF in 50% yield.[7] Other oxidation conditions were filed in the Chinese patents.[5]

BAFF was hardly converted into BNFF in the reaction with less than 30% H_2O_2 even in the presence of various additional oxidants, while the reaction with more than 50% H_2O_2, H_2SO_4 and ammonium persulfate or TFAA proceeded in considerable yield. As higher the concentration of H_2O_2 in addition to oxidants and strong acids, better yield was given. The reaction with ammonium persulfate was slower than that with TFAA, but the yield was almost same. In a scale up process, less than 60% of H_2O_2 and ammonium persulfate were preferred.

Next, we were focused on the oxidation reaction of BAFOZ (**4**) to BNFOZ (**6**). The oxidation took place under the same oxidation condition (Scheme **2**), and was confirmed by IR and ^{13}C NMR.

BNFOZ was obtained in moderate yield, but the reaction was harder to control, compared with that of BAFF. One of the reasons was that BNFOZ was slightly more unstable than BNFF in thermal property.

The crystal density was calculated as 1.745 for BAFOZ and 1.883 for BNFOZ.[13] These figures were slightly smaller

BAFF (3)   **BAFOZ (4)**

oxidation   oxidation

BNFF (5)   **BNFOZ (6)**
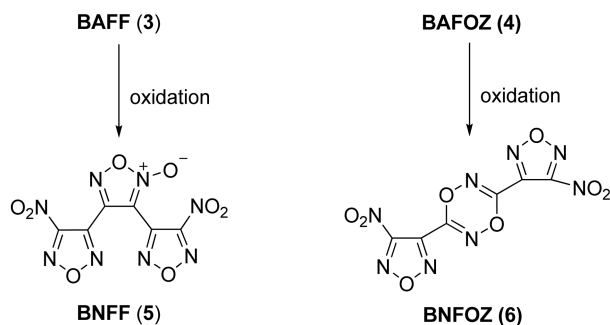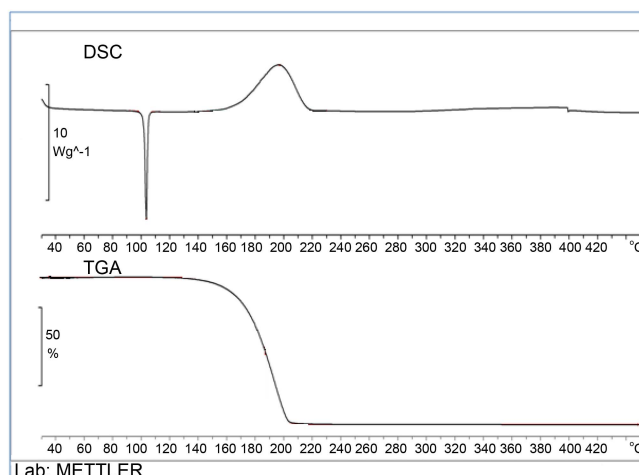
Scheme 2. A Synthesis of BNFF and BNFOZ.

Figure 1. DSC and TGA of BNFOZ.

than those of furoxan isomers. As shown in Figure 1, the DSC curve for BNFOZ showed that an endothermic peak began at its melting point (101.64 °C) with summit peak at 103.33 °C, and a major exothermic peak at 196.66 °C. The TGA curve showed that BNFOZ was rather volatile in molten state.

In conclusion, BAFF and BAFOZ were prepared in the dimerization reaction of the corresponding nitrile oxide, derived from chloroxime **1**. Depending on the reaction media, BAFF or BAFOZ was selectively given as a major compound using the same base. Under the same oxidation conditions, BAFF and BAFOZ can be oxidized to BNFF and BNFOZ respectively, but the reaction of BAFOZ was more difficult, because of its thermal stability. On the basis of the thermal properties of DSC and TGA, BNFOZ was more volatile and its melting point was lower than that of BNFF.

Experimental Section

General. ^{1}H/^{13}C NMR spectra were recorded on Varian Oxford 200 or Unityinova 400 instruments. Melting points were performed on recrystallized solids and recorded on a SRS OptiMelt or electrothermal 9100 melting point apparatus and were uncorrected.

Caution: Furazan and furoxan derivatives are suspected explosive. In addition to these compounds, H_2O_2-H_2SO_4 should be treated with appropriate precautions.

3,6-Bis(4-amino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (BAFOZ, 4). To a solution of chloroxime **1** (6.50 g, 0.026 mol) in THF (80 mL) was added dropwise 3% aq. K_2CO_3 (69 mL, 0.030 mol) for 30 min. The reaction mixture was standing for 2 h below 10 °C, and filtered to give a white solid (3.45 g, 69%). mp 230-233 °C (dec.)[8b]; IR (KBr) 3456, 3323, 1640, 1609, 1533, 1106, 1028 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.54 (bs); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 155.0, 153.5, 136.0.

3,6-Bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (BNFOZ, 6). To a solution of BAFOZ (1.0 g, 4.0 mmol) and ammonium persulfate (3.75 g, 16.4 mmol) in c-H_2SO_4 (16 mL) was added 60% H_2O_2 (10.0 mL, 0.256 mol) dropwise.

The mixture was stirred at below 10 °C for 1 h, and then 50 °C for 4 h. The precipitate was filtered to give a white solid (0.74g, 60%). mp 102-104 °C; IR (KBr) 1587, 1556, 1359, 1273, 1088, 1030 cm^{-1}; ^{13}C NMR (DMSO-d_6, 100 MHz) δ 160.4, 153.7, 140.4. Anal Calcd: C, 23.09; N, 35.90. Found: C, 23.37; N, 34.69.

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