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13. ABSTRACT *(Maximum 200 words)*

The reaction of glyoxime (4) and hydroxylamine hydrochloride in aqueous sodium hydroxide was found to be a safe and inexpensive method for the preparation of multigram quantities of diaminoglyoxime (5). Potassium hydroxide mediated dehydration of 5 furnished diaminofurazan (1) in good yield of exceptional purity. The ready availability of 1 and 5 has facilitated the synthesis of new energetic furazan derivative MNOTO (8).

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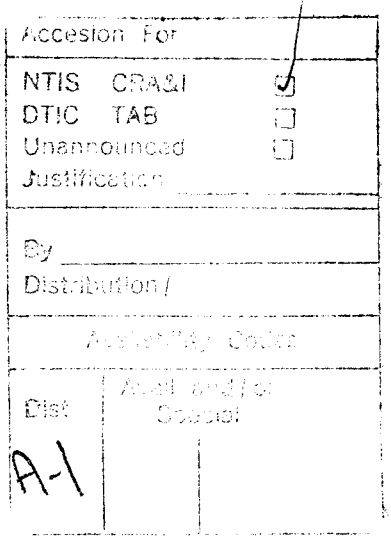

A Convenient Synthesis of Diaminoglyoxime and Diaminofurazan: Useful Precursors for the Synthesis of High Density Energetic Materials.

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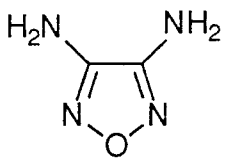
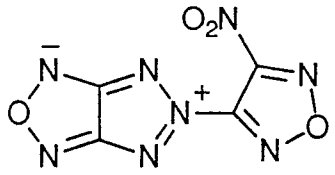
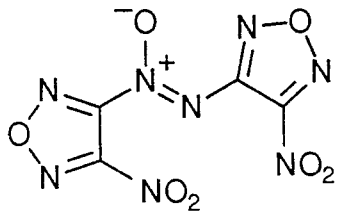
During the course of recent studies directed toward the synthesis of new energetic materials, the furazan ring has been found to be a useful substructure for the design of new high density, high energy materials composed exclusively of carbon, hydrogen, nitrogen and oxygen atoms. [1] The diaminofurazan (**1** *DAF*) has been shown to be a useful precursor for the construction of high energy furazan derivatives *NOTO* (**2**) and *DNAF* (**3**). [2,3] However, the preparation of *DAF* (**1**) has been limited by the availability of the precursor diaminoglyoxime (**5** *DAG*). There are several reports in the literature which describe methods for the synthesis of *DAG* (**5**). [4–8] However, these procedures require the use of obscure starting materials and hazardous or expensive reagents. Herein we wish to report a facile inexpensive method for the multigram synthesis of *DAG* (**5**) and *DAF* (**1**). In addition, the availability of useful quantities of these intermediates has facilitated the synthesis of a new energetic furazan derivative.



1



2 (*NOTO*)

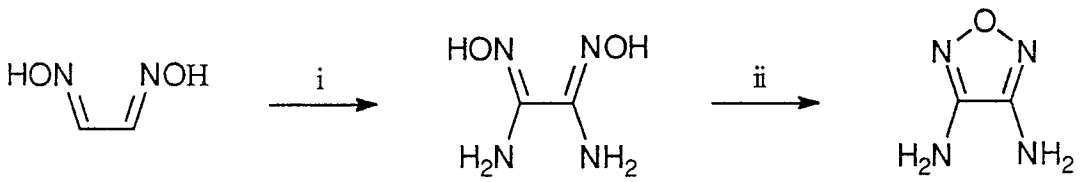


3 (*DNAF*)

RESULTS AND DISCUSSION

As illustrated in Scheme 1, the synthesis of *DAF* (**1**) was achieved in two steps from readily available glyoxime **4**. [8] The key intermediate *DAG* (**5**) was prepared from the reaction of **4** and hydroxylamine hydrochloride in an alkaline aqueous sodium hydroxide solution at 90 °C. This conversion, originally described without experimental details in a Russian patent, afforded *DAG* (**5**) in 60% yield. [9] This procedure represents an improvement over the methods previously reported in that it avoids the use of cyanogen gas and *DAG* (**5**) can be obtained from commercially available reagents in good yield at low cost.

Scheme 1



4 **5** **1**

Reagents: i) $NH_2OH{\cdot}HCl$, NaOH (aq), 60 °C. ii) KOH (aq), 170 °C, stainless steel reactor.

The generation of furazan from the dehydration of glyoxime (**4**) at elevated temperatures in aqueous sodium hydroxide has been known for nearly a century. [10] However, the efficient dehydration of *DAG* (**5**) in aqueous sodium hydroxide has been shown to require higher temperatures in a sealed reaction vessel. [11,12] In this study it was found that a simple stainless steel reactor could be employed to safely and easily perform the dehydration reaction of *DAG* (**5**) on a multigram scale to furnish *DAF* (**1**). Both sodium hydroxide and potassium hydroxide were found to effect the dehydration reaction; however, potassium hydroxide routinely furnished *DAF* (**1**) in high yield (> 70%) in a state of exceptionally high purity (Scheme 1).

With the *DAF* (**1**) in hand, attention turned toward the synthesis of new high density energetic compounds. Based on the detonation performance of the

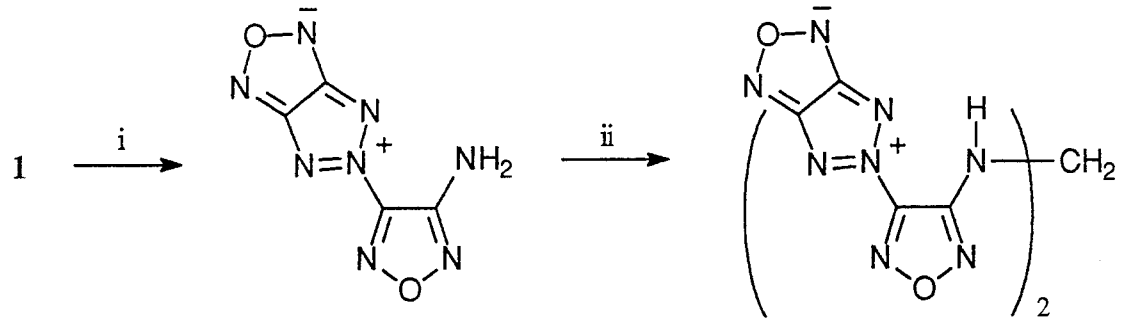
furazan derivatives *NOTO* (**2**) and *DNAF* (**3**) [2,3], previously synthesized in these laboratories, the 5,5′-[methanedinitramino-bis(1,2,5-oxadiazol-4,3-diyl]bis[1*H*-[1,2,3]triazolo-[4,5-*c*][1,2,5]oxadiazolium]bis-(inner salt) (**8** *MNOTO*) was viewed as an attractive synthetic target. Excellent calculated density (d) and detonation properties [detonation velocity (D) and detonation pressure (P_{CJ})] suggested that *MNOTO* (**8**) could be useful as a new solid state explosive or propellant (Scheme 2). [13]

As illustrated in Scheme 2, the synthesis of *MNOTO* (**8**) proceeded from *DAF* (**1**) through the intermediate 5-(4-amino-1,2,5-oxadiazol-3yl)-1*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazolium inner salt (**6** *AMOTO*). *AMOTO* (**6**) was prepared from *DAF* (**1**) using a two step procedure previously reported. [3] Condensation of *AMOTO* (**6**) with formaldehyde furnished the 5,5′-[methanediamino-bis(1,2,5-oxadiazol-4,3-diyl)]bis[1*H*-[1,2,3]triazolo[4,5-*c*]-[1,2,5]oxadiazolium]-bis(inner salt) (**7** *MAOTO*) in 90% yield. *MAOTO* (**7**) was calculated to possess fair detonation properties and a density of 1.81 g/cm^3. The compound was found to be thermally stable above 200 °C and shock insensitive (no detonation with a hammer blow).

The *N*-nitration of the amine nitrogen atoms to give *MNOTO* (**8**) was achieved in a mixture of 100% HNO_3 and acetic anhydride. This provided *MNOTO* (**8**) in 97% yield as a colorless amorphous solid. As expected the detonation properties of *MNOTO* (**8**) were greatly enhanced over those of *MAOTO* (**7**). *MNOTO* (**8**) was found to be an impact sensitive material which exploded violently with flame when struck by a hammer. In addition, the thermal stability of *MNOTO* (**8**) was found to be less than that observed for *MAOTO* (**7**) and furazan derivatives *NOTO* (**2**) and *DNAF* (**3**). [2,3]

In summary, *DAF* (**1**) has again been shown to be a useful precursor for the synthesis of energetic compounds. With a convenient and inexpensive preparation of *DAG* (**5**) and *DAF* (**1**) now available, large-scale synthesis of furazan derivatives are now economically feasible. In addition, the ready availability of *DAF* (**1**) should lead to the development of new furazan based compounds.

Scheme 2



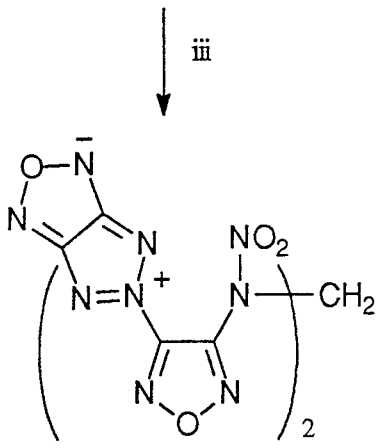
AMOTO **6**

MAOTO **7**

d = 1.81 g/cm^3

D = 8.54 mm/μsec

P_{CJ} = 340 kbar



MNOTO **8**

d = 1.90 g/cm^3

D = 9.25 mm/μsec

P_{CJ} = 407 kbar

Reagents: i) See conditions cited in Reference 3. ii) 37% H_2CO, HCl, 100 °C.
iii) 100% HNO_3, Ac_2O, – 5 ° to 15 °C.

EXPERIMENTAL

All chemicals were purchased from Aldrich Chemical Company, Milwaukee, WI. ^1H and ^{13}C nmr spectra were obtained on a Varian–Gemini Multiprobe 300 MHz nmr spectrometer and

ir spectra were recorded on a Perkin–Elmer 1600 series infrared spectrometer. Melting points were determined on a Mel – Temp II and are reported uncorrected. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN and Midwest Micro Lab, Indianapolis, IN. An inexpensive stainless steel reactor was made in the Machine Shop at the University of New Orleans. [14] *Caution*: *MNOTO* (**8**) should be treated as dangerously explosive.

Diaminoglyoxime (**5**).

Aqueous sodium hydroxide (100 mL, 5 M) was added to glyoxime (**4**) (17.6 g, 0.2 mol) and stirred in a 250 mL round bottom flask. Hydroxylamine hydrochloride (27.8 g, 0.4 mol) was then added in one portion. The flask was fitted with a condenser and heated in an oil bath (keeping the bath temperature at 90 °C for 6 h). The reaction mixture was allowed to cool to room temperature and a colorless crystalline solid (needles) precipitated. The isolated solid was washed with cold water (10 – 15 mL) and dried to give diaminoglyoxime (**5**), 14.0 g (60%), mp 203–205 °C (dec) (water), lit mp 203 °C [6]. ^{1}H nmr (dimethylsulfoxide–d_6): δ 5.18 (bs, 4H, NH_2), 9.76 (s, 2H, OH). ^{13}C nmr (dimethylsulfoxide–d_6): δ 145.2.

Diaminofurazan (**1**).

A suspension of diaminoglyoxime (**5**) (23.6 g, 0.2 mol) in aqueous potassium hydroxide (80 mL, 2 M) was placed in a stainless steel reactor. The reactor was closed and placed in an oil bath preheated to 170 – 180 °C and maintained at that temperature for 2 h. The reactor was cooled by immersion in an ice bath for 2 h and opened in a hood to avoid contact with trace amounts of ammonia as it escaped. The mixture was removed by washing the chamber with water (2 × 20 mL) and filtered to give **1** as colorless needles, 14.1 g (70%), mp 179 – 180 °C, lit mp 180 °C [11]; ir (potassium bromide): 3423, 3318, 1647, 1591, 1353 cm^{-1}. ^{1}H nmr (dimethylsulfoxide–d_6): δ 5.81 (bs, 4H, NH_2). ^{13}C nmr (dimethylsulfoxide–d_6): δ 149.7.

5,5'-[Methanediamino-bis(1,2,5-oxadiazol-4,3-diyl)]bis[1H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazolium]-bis(innersalt) (**7**).

To a suspension of *AMOTO* (**6**) (1.0 g, 5.2 mmol) in water (20 mL), an aqueous solution of formaldehyde (37%, 0.2 g, 2.6 mmol) and 3 drops of hydrochloric acid (12 M) were added and the mixture refluxed for 2 h. The mixture was then cooled and filtered to furnish a yellow solid which was washed with cold water and dried under vacuum to give **7**, 0.94 g (90%), mp 244 – 245 °C (dec) (DMF/water); ir (potassium bromide): 3410, 1618, 1572, 1046, 1202 cm^{-1}. ^1H nmr (dimethylsulfoxide – d_6): δ 5.09 (bs, 2H, CH_2), 7.89 (bs, 2H, NH); ^{13}C nmr (dimethylsulfoxide–d_6): δ 165.4, 150.6, 145.3, 53.8.

Anal. Calcd for $C_9H_4N_{16}O_4$: C, 27.01; H, 1.01; N, 55.99. Found: C, 26.91; H, 1.08; N, 55.73.

5,5'-[Methanedinitramino-bis(1,2,5-oxadiazol-4,3-diyl)]bis[1H-[1,2,3]triazolo[4,5-c][1,2,5]-oxadiazolium]-bis(innersalt) (**8**).

To a solution of 100% HNO_3 (1.5 g) and acetic anhydride (1.0 g) at 0 °C was added **7** (1.0 g, 2.5 mmol) in one portion. The reaction mixture was stirred for 30 min then allowed to warm to 10 – 15 °C with continued stirring for 30 min. The mixture was then poured onto crushed ice (100 g). A colorless precipitate was collected and washed with cold water to give **8**, 1.2 g (97%), mp 160 °C (dec) (dichloromethane); ir (potassium bromide): 1608, 1282, 1103, 1038. ^1H nmr (dimethylsulfoxide – d_6): δ 7.10 (s, 2H, CH_2); ^{13}C nmr (dimethylsulfoxide – d_6): δ 166.9, 151.4, 147.0, 67.2.

Anal. Calcd for $C_9H_2N_{18}O_8$: C, 22.05; H, 0.41; N, 51.43. Found: C, 21.97; H, 0.42; N, 51.28.

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[1] For a review on the chemistry of energetic materials see A.T. Nielsen, Chemistry of Energetic Materials, G.A. Olah and D.R. Squire, eds, Academic Press, Inc., San Diego, CA, **1991**, p 95 and references cited therein.

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[13] We are grateful to Dr. Richard Hollins, Naval Weapons Center, China Lake, CA for providing a computational method to calculate d, D and P_{CJ} for structural formula restricted to C, H, N, O and F atoms. Target values of $d \approx 2.0$ g/cm^3, $D \approx 10$ mm/μsec, $P_{CJ} \approx 400$ kbar.

[14] Detailed specifications for the stainless steel reactor are available upon request.

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