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Dense Compounds of C, H, N, and O Atoms: Nitramine Derivatives of Diimino- and Dioxodecahydro-1*H*,5*H*-Diimidazo-[4,5-*b*:4′,5′-*e*]pyrazine

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ABSTRACT

Guanidine condensed with 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine **1** *to give 2,6-diiminodecahydro-1*H,5H*-diimidazo*[4,5-b:4′,5′-e]*pyrazine* **3** *isolated as the tetrahydrochloride salt. Nitric acid (100%) at −40°C converted the bisguanidine* **3** *to 2,6-dinitrimino-4,8-dinitrodecahydro-1*H,5H*-diimidazo*[4,5-b:4′,5′-e]*-pyrazine* **8** *isolated as a dihydrate, whereas nitration by nitronium tetrafluoroborate at 0° to 25°C afforded 2,6-diimino-4,8-dinitrodecahydro-1*H,5H*-diimidazo*[4,5-b:4′,5′-e]*pyrazine* **9** *isolated as the monohydrated bistetrafluoroborate salt, and treatment with nitric acid (100%) and acetic anhydride or phosphorus pentoxide converted the bisguanidine* **3** *to 2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1*H,5H*-diimidazo*[4,5-b:4′,5′-e]*pyrazine* **4**, *also obtained from the tetra* N*-nitro compound* **8** • 2 H_2O *and from the dinitramine* **9** • 2 HBF_4 • H_2O *after similar treatment. The cis-syn-cis- configuration of the tricyclic bisurea* **4** *and bisguanidine* **9** *was confirmed by X-ray crystallographic analysis. Nitrosation by nitrous acid or by dinitrogen tetroxide converted the bisguanidine* **3** *to a hydrated 2,6-dinitrosimino-4,8-dinitrosodecahydro-1*H,5H*-diimidazo*[4,5-b:4′,5′-e]*pyrazine* **10** • 2.5 H_2O, *whereas treatment with nitrosonium tetrafluoroborate afforded the bistetrafluoroborate salt of 4,8-dinitroso derivative* **11** • 2 *HBF4. The nitrosamines* **10** *and* **11** *were converted to the tetranitro compound* **8** • 2 H_2O *on treatment with nitric acid (100%) at −40°C. Treatment with fluoroboric acid etherate in acetonitrile converted nitroimino groups in compound* **8** • 2 H_2O *and nitrosimino groups in compound* **10** • 2.5 H_2O *to imino groups in compounds* **9** • 2 HBF_4 • H_2O *and* **11** • 2 HBF_4 *respectively.*

INTRODUCTION

In a continuing search [1, 2] for dense [3] ($d \sim 2.0$) energetic compounds restricted in composition to C, H, N, and O atoms the pernitro derivatives **4** [2] (calcd. d 2.04) and **5** (calcd. d 2.01) of 2,6-dioxodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4′,5′-*e*]pyrazine **2** and the corresponding 2,6-diimino derivative **3** and 2,6-dioxo-2,3,4,6,7,8-hexahydro-1,3,4,5,7,8-hexanitro-1*H*,5*H*-diimidazo[4,5-*b*:4′,5′-*e*]pyrazine **6** (calcd d 2.14) were sought (Scheme 1). In previously reported one-step operations 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine **1** (from formamide and glyoxal) was converted to the caged dinitramine **7** (d 1.97 by the flotation method, calcd. d 1.94) on treatment with glyoxal and nitric acid in sulfuric acid [4] and to the bisurea **2** on treatment with urea [2]. The *cis-syn-cis-* conformation of the tricyclic structure was determined by X-ray diffraction for each of two tetra-*N*-nitro derivatives [2] and the hexa-*N*-nitro derivative **4** • CH_3CN [5] of the bisurea **2** and was assumed for the unsubstituted bisurea **2** and its other *N*-nitro and *N*-nitroso derivatives since isomerization under the conditions of nitration and nitrosation was considered to be unlikely [2]. The

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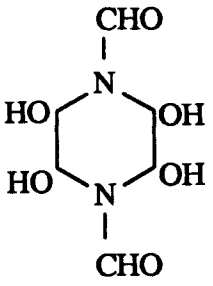

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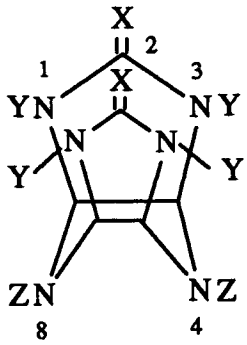


2 X = O, Y = Z = H

3 X = NH, Y = Z = H

4 X = O, Y = Z = NO_2

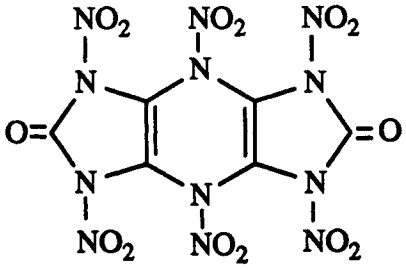
5 X = NNO_2, Y = Z = NO_2

8 X = NNO_2, Y = H, Z = NO_2

9 X = NH, Y = H, Z = NO_2

10 X = NNO, Y = H, Z = NO

11 X = NH, Y = H, Z = NO



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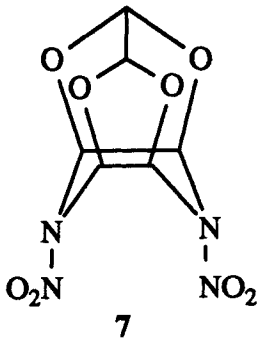


7

SCHEME 1

discovery of these condensation reactions led to further examination of the reactive hemiamidal **1**.

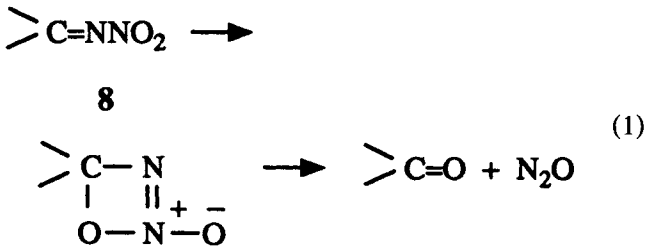
The preparation and properties of the bisguanidine **3** and its *N*-nitro and *N*-nitroso derivatives are reported here. A *cis-syn-cis-* conformation of the bisguanidine **3** and its *N*-nitro- and *N*-nitroso- derivatives was asigned on the assumption that similar structures were afforded by the condensations of urea and of guanidine with the hemiamidal **1** and on an X-ray diffraction study [5] of a di-*N*-nitro derivative (below) of the bisguanidine **3**.

RESULTS AND DISCUSSION

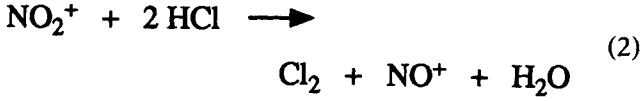
A combination of guanidine hydrochloride and the *meso*-tetrahydroxypiperazine **1** (axial *trans*-hydroxyl groups at positions 2,3 and 5,6 [2]) afforded 2,6-diiminodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4′,5′-*e*]pyrazine **3** as a tetrahydrochloride derivative, a structure in agreement with ^{1}H NMR signals at δ 5.01 for the four methine protons and δ 5.18–6.40 for the remaining protons (8 NH and 4 HCl) exchangeable with D_2O, ^{13}C NMR signals at δ 158.18 (C=N) and δ 63.04 (four CH at positions 3a, 4a, 7a, and 8a), and EI-MS values at *m/z* 59 and 43 known to be characteristic of other guanidine moieties [6]. Attempts to condense the hemiamidal **1** with nitroguanidine and with amidines were unsuccessful.

The tetrahydrochloride of the bisguanidine **3** was treated with (1) nitric acid (100%) neat and in combination with acetic anhydride or phosphorus pentoxide and (2) nitronium tetrafluoroborate. At −40°C the bisguanidine **3** in nitric acid (100%) was converted to a tetranitro derivative isolated as a dihydrate. The assigned structure of 2,6-dinitrimino-4,8-dinitrodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4′,5′-*e*]pyrazine **8** • 2 H_2O was in agreement with ^{1}H NMR singlets at δ 6.94 (CH), δ 8.44, and δ 9.67 (NH and OH), the detection of ^{13}C NMR signals at

δ 158.31 and δ 64.28 for two sets of carbon atoms (see above), and by a principal EI-MS peak at *m/z* 44 ascribed to dinitrogen oxide, presumably produced by fragmentation following an isomerization of the nitrimine to an intermediate oxadiazete derivative, Equation (1) [7].

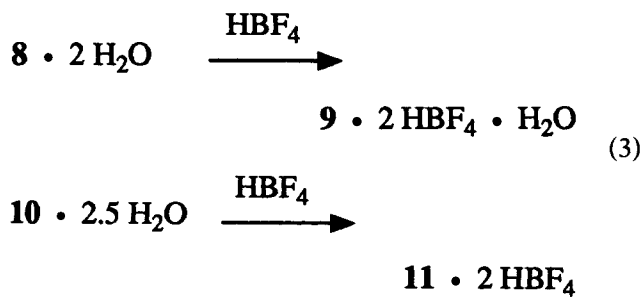


(1)



(2)

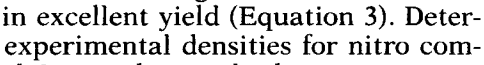
Treatment with nitronium tetrafluoroborate converted the tetrahydrochloride of the bisguanidine **3** to the 4,8-dinitro derivative **9** isolated as a monohydrate of the bistetrafluoroborate salt, a structure supported by the detection of ^{13}C NMR signals at δ 157.88 and δ 63.78 and by X-ray diffraction [5]. Presumably the presence of water needed for hydration was brought about by a reaction between the nitronium salt and hydrogen chloride (Equation 2) in a variation of the Aqua Regia system [8]. Further support for the assignment was found in the conversion of the tetranitro derivative **8** • 2 H_2O to the dinitro derivative **9** • 2 HBF_4 • H_2O on similar treatment with nitronium tetrafluoroborate. Presumably this unusual conversion of a nitrimine **8** • 2 H_2O to an imine **9** • 2 HBF_4 • H_2O depended on a new reaction with (adventitious) fluoroboric acid. In a separate experiment the tetranitro derivative **8** • 2 H_2O was treated with fluoroboric acid etherate in acetonitrile to give the diimine **9** • 2 HBF_4 • H_2O in excellent yield (Equation 3). Determination of experimental densities for nitro compounds **8** and **9** was thwarted when attempts to liberate each from its complex was unsuccessful; the respective calculated densities [3] of 1.87 and 1.75 revealed the necessity for further nitration, so far unsuccessful, to meet the goal of $d > 2.0$. The preparation of the unsaturated hexanitro bisurea **6** is under investigation.



(3)

In the presence of acetic anhydride or phosphorus pentoxide nitric acid (100%) converted the bisguanidine **3** • 4 HCl to the 1,3,4,5,7,8-hexanitro derivative **4**, of the bisurea **2**. The pernitro compound **4** was also obtained from the tetra *N*-nitro compound **8** • 2 H_2O and from the dinitramine **9** • 2 HBF_4 • H_2O by similar treatment with nitric acid (100%) and acetic anhydride. An intermediate 2,6-dinitrimino-1,3,4,5,7,8-hexanitrodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4′,5′-*e*]pyrazine **5**, rather than the bisurea **2** or any one of its *N*-nitro derivatives, was assumed to be the precursor to the pernitrobisurea **4** since the treatment of the bisurea **2** with nitric acid (100%) in acetic anhydride at 0–25°C gave two tetra- and impure penta-*N*-nitro derivatives without a trace of the hexanitro compound **4** [2]. Differentiation between various available routes for the presumed conversion of the bisguanidine **5** to the bisurea **4** and previously known conversions of other 2-iminoimidazolidine moieties to imidazolidin-2-one moieties [9] by treatment with nitric acid was not attempted. The *cis-syn-cis* structure of the tricyclic bisurea **4** was confirmed by an X-ray crystallographic analysis [5].

The tetrahydrochloride of the bisguanidine **3** was converted to a tetranitrosamine by treatment with either nitrous acid or dinitrogen tetroxide. After workup the product in each reaction was isolated as a hydrate and was assigned the structure of 2,6-dinitrosimino-4,8-dinitrosodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4′,5′-*e*]pyrazine **10** • 2.5 H_2O. The structure assignment was based on the detection of ^{13}C NMR signals at δ 158.51 (C=N) and the pair δ 68.37 and δ 56.28 (four CH) and by analogy with the structure of the nitration product **8**. Presumably the source of water needed for hydration was provided by an interaction between dinitrogen tetroxide and hydrogen chloride (Equation 4) [10]. The conversion of the tetranitroso compound **10** • 2.5 H_2O to the tetranitro compound **8** • 2 H_2O by treatment with nitric acid (100%) was straightforward.



(4)

Nitrosation by treatment with nitrosonium tetrafluoroborate followed by treatment with water gave a dinitroso derivative, isolated as a bistetrafluoroborate salt of 2,6-diimino-4,8-dinitrosodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4′,5′-*e*]pyrazine **11** • 2 HBF_4, an assignment supported by the detection of ^{13}C NMR signals at δ 157.86, δ 67.85, and δ 55.30 (see above) [11] and by conversion to the tetranitro compound **8** • 2 H_2O on treatment with nitric acid (100%). The dinitrosamine **11** • 2 HBF_4 was also obtained from the tetranitroso compound **10** • 2.5 H_2O by treatment with fluoroboric acid etherate in acetonitrile, in an example of a new efficient conversion of a nitrimine to an imine (Equation 3). It is noteworthy that fluoroboric acid did not affect the two nitrosamino centers in the tetranitroso compound **10** • 2.5 H_2O. In a recent report denitrosation of cyclic *N*-nitrosamines was brought about

by treatment with boron trifluoride complexes in the presence of sodium bicarbonate [12].

EXPERIMENTAL

Spectral data were obtained from the following instruments: Pye-Unicam SP 200 IR; JEOL FX 90 Q NMR, Hewlett-Packard 5985 (70 eV) (GC-MS). ^{1}H NMR spectra were run in deuterated solvents with tetramethylsilane as an internal standard. ^{13}C NMR were recorded at 22.5 MHz with the deuterated solvent as an internal reference. The central peak of the solvent multiplet signal was assigned: δ 77.00 ($CDCl_3$), δ 39.50 $(CD_3)_2(SO)$, and δ 29.8 $(CD_3)_2(CO)$. Melting points were determined on a MEL-TEMP II melting point apparatus and are uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, IN, and Galbraith Laboratories, Knoxville, TN. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel (various grades). IR spectroscopic analyses supported assigned molecular structures. The reported EI-MS data were restricted to major *m/z* values and to M^+ when detected. 1,4-Diformyl-2,3,5,6-tetrahydroxypiperazine **1** was obtained from a condensation between formamide and glyoxal [13]. Mixtures of nitric acid and acetic anhydride and each *N*-nitro compound must be regarded as potentially explosive.

*2,6-Diiminodecahydro-1*H,5H-*diimidazo-*[*4,5*-b:*4',5'*-e]*pyrazine* **3**

To a stirred solution of guanidine hydrochloride (9.5 g, 0.1 mol) in concentrated hydrochloric acid (25 mL) 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine **1** (4.1 g, 0.02 mol) was added in portions over a period of 15 min. The reaction mixture was stirred at 25°C for 17 h. A solid was isolated, washed with alcohol (3 × 30 mL), and dried to give the bisguanidine **3** as the tetrahydrochloride derivative (3.6 g, 53%), mp 168–170°C (dec) (concentrated hydrochloric acid/alcohol). ^{1}H NMR (DMSO-d_6): δ 5.01 (s, 4H, CH), 5.18–6.40 (m, 12H, exchanged with D_2O); ^{13}C NMR (DMSO-d_6): δ 158.18, 63.04; EI-MS, *m/z* (relative intensity): 136 (100), 59 $(CH_5N_3)^+$ (82), 43 $(CH_3N_2)^+$ (93), and 36 (84). Anal. Calcd. for $C_6H_{16}N_8Cl_4$: C, 21.06; H, 4.68; N, 32.76. Found: C, 21.20; H, 4.90; N, 32.51.

*2,6-Dinitrimino-4,8-dinitrodecahydro-1*H,5H-*diimidazo*[*4,5*-b:*4',5'*-e]*pyrazine* **8**

2, 6-Diiminodecahydro-1*H*, 5*H*-diimidazo[4, 5-*b*:4', 5'-*e*]pyrazine tetrahydrochloride (3.0 g, 9.0 mmol) was added in portions to a stirred solution of nitric acid (100%) (60 mL), at −40°C; the mixture was stirred for 1 h and poured onto ice. A solid separated on standing (1 h). It was isolated and washed with ice-cold water. The colorless powder was dissolved in dimethyl sulfoxide and reprecipitated with chloroform to give the product **8** as a dihydrate (2.3 g, 70%), mp 220–222°C (explosive dec). ^{1}H NMR (DMSO-d_6): δ 6.95 (s, 4H, CH), 8.44 (bs, 4H), 9.67 (bs, 4H) for NH and OH; ^{13}C NMR (DMSO-d_6): δ 158.31, 64.28; EI-MS, *m/z* (relative intensity): 368 (M^+ − 44 (N_2O)) (1.6) and 44 $(N_2O)^+$ (100). Anal. Calcd. for $C_6H_{12}N_{12}O_{10}$: C, 17.48; H, 2.91; N, 40.78; O, 38.83. Found: C, 17.58, H, 3.00; N, 40.04; O, 37.36.

*2,6-Diimino-4,8-dinitrodecahydro-1*H,5H-*diimidazo*[*4,5*-b:*4',5'*-e]*pyrazine* **9**

Nitronium tetrafluoroborate (4.0 g, 30 mmol) in acetonitrile (40 mL) was added in portions with stirring to the tetrahydrochloride (1.0 g, 3 mmol) of the bisguanidine **3** at 0°. Stirring was maintained for 1 h at 0°C and 17 h at 25°C. After solvent removal recrystallization (acetonitrile/chloroform) of the residue gave the product **9** isolated as a monohydrated bistetrafluoroborate salt, a colorless crystalline solid (0.75 g, 55%), mp 250–255°C (dec). ^{1}H NMR (acetone-d_6): δ 7.36 (s, 6H, CH, and NH), 8.10 (bs, 4H) and 8.99 (bs, 4H, NH, and H_2O); ^{13}C NMR (acetone-d_6): δ 157.88, 63.78. Anal. Calcd. for $C_6H_{14}N_{10}O_5B_2F_8$: C, 15.01; H, 2.92; N, 29.19; O, 16.68; B, 4.50; F, 31.69. Found: C, 15.21; H, 2.83; N, 28.80; B, 4.52; F, 31.48. Lower yields (37% and 28%) were obtained when the reaction was carried out at 50°C and 80°C for 3 h. The dinitramine **9** • 2 HBF_4 • H_2O (70%) was also obtained from a similar reaction at 0–25°C between nitronium tetrafluoroborate and the dihydrate of the tetranitro compound **8**.

*2,6-Dioxo-1,3,4,5,7,8-hexanitrodecahydro-1*H,5H-*diimidazo*[*4,5*-b:*4',5'*-e]*pyrazine* **4**

(a) To a solution of nitric acid (100%) (30 mL) 2,6-diiminodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]-pyrazine tetrahydrochloride **3** • 4 HCl (2.0 g, 6.0 mmol) was added with stirring in small portions at 0°C. The mixture was stirred for 15 min, acetic anhydride (30 mL) was added dropwise at 0°C, and stirring was continued for 1 h at 0–5°C and 17 h at 25°C. A precipitate was collected, washed with ice water (3 × 10 mL), and dried to give the hexanitro bisurea **4** (1.4 g, 52%) as a colorless solid, mp 208–210°C (explosive dec) (acetonitrile-chloroform) [2]. It was purified by recrystallization from a mixture of acetonitrile and chloroform. Anal. Calcd. for $C_6H_4N_{12}O_{14}$: C, 15.38; H, 0.85; N, 35.90; O, 47.86. Found: C, 15.66; H, 0.89; N, 35.30; O, 46.72.

(b) Phosphorus pentoxide (45 g) was slowly added to nitric acid (100%) (90 mL) with stirring under nitrogen and cooling in an ice water bath to keep the temperature of the solution below 30°C. A clear yellow solution developed over a period of 40 min. The stirred solution was cooled to −15°C and kept below −10°C as the tetrahydrochloride (2.0 g, 6.0

mmol) of the bisguanidine **3** was added in portions over 30 min. The mixture warmed to 25°C over 1.5 h. It was maintained at this temperature for 30 min, at 35°C (bath temperature 40°C) for 1 h, at 45°C (bath temperature 50°C) for 2 h, and stirred into ice water (250 mL). The precipitate was collected, washed with cold water and methylene chloride, and dried to give the hexanitro bisurea **4** [2], 1.85 g (68%).

(c) 2,6-Dinitrimino-4,8-dinitrodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4′,5′-*e*]pyrazine **8** as a dihydrate (1.5 g, 4.0 mmol) was added in small portions at 0°C with stirring to nitric acid (100%) (20 mL). The mixture was stirred for 15 min, acetic anhydride (20 mL) was added dropwise at 0°C, and stirring was continued for 1 h at 0–5°C and at 17 h at 25°C. A precipitate was collected, washed with chloroform (3 × 15 mL) and dried to give the hexanitro derivative **4** [2], 1.4 g (82%).

(d) Nitric acid (100%) in acetic anhydride at 0–25°C converted the dinitramine **9** • 2 HBF_4 • H_2O to the hexanitrobisurea **4** (77%).

*2,6-Dinitrosimino-4,8-dinitrosodecahydro-1*H,5H-*diimidazo*[4,5-b:4′,5′-e]*pyrazine* **10**

(a) Sodium nitrite (6.9 g, 0.1 mole) and hydrochloric acid (18%) (20 mL) were added at 0°C with stirring to the tetrahydrochloride (1.7 g, 5.0 mmol) of the bisguanidine **3** in water (20 mL) and the mixture was stirred at 0°C for 30 minutes. The tetranitroso bisguanidine **10** • 2.5 H_2O was isolated and reprecipitated (dimethyl sulfoxide/chloroform) to give a colorless solid (0.24 g, 13%), mp 204–206°C (explosive dec). ^{1}H NMR (DMSO-d_6): δ 6.54–7.34 (m, 4H, CH), 8.40–8.62 (m, 4H, NH exchangeable with D_2O), 9.61 (bs, 5H, H_2O, exchangeable with D_2O); ^{13}C NMR (DMSO-d_6): δ 158.51, 68.37, 56.28. Anal. Calcd. for $C_6H_{13}N_{12}O_{6.5}$: C, 20.16; H, 3.64. Found: C, 20.38; H, 3.39. Nitric acid (100%) at −40°C converted the tetranitroso compound **10** • 2.5 H_2O to the tetranitro compound **9** • 2 H_2O (63%).

(b) To dinitrogen tetroxide (20 mL) the tetrahydrochloride (2.4 g, 7.0 mmol) of the bisguanidine **3** was added in portions with stirring at −10°C. The mixture warmed to 25°C and was stirred for 17 h. The tetranitroso derivative **10** • 2.5 H_2O (2.4 g, 90%) precipitated and was isolated by trituration with ether (4 × 15 mL).

*2,6-Diimino-4,8-dinitrosodecahydro-1*H,5H-*diimidazo*[4,5-b:4′,5′-e]*pyrazine* **11**

The tetrahydrochloride (1.7 g, 5.0 mmol) of the bisguanidine **3** was added in portions at 0°C with stirring to nitrosonium tetrafluoroborate (5.0 g, 42 mmol) in anhydrous acetonitrile (30 mL). After stirring at 0°C for 1 h and at 25°C for 17 h and after treatment with cold water (1.0 mL) solvent removal left a residue. Recrystallization (acetonitrile/chloroform) gave the pyrazine **11** • 2 HBF_4 (0.6 g, 53%), mp 199–201°C (dec). ^{1}H NMR (DMSO-d_6): δ 6.90–7.73 (m, 4H, CH), 8.06–8.95 (m, 8H, NH); ^{13}C NMR (DMSO-d_6): δ 157.8, 67.85, 55.30. Anal. Calcd. for $C_6H_{12}N_{10}O_2B_2F_8$: C, 16.74; H, 2.79; N, 32.58. Found: C, 17.10; H, 2.87; N, 32.71. Nitric acid (100%) at −40°C converted the dinitrosamine **11** to the tetranitro compound **8** • 2 H_2O (66%).

Denitration and Denitrosation with Fluoroboric Acid Etherate

A mixture of the tetranitro compound **8** • 2 H_2O (0.24 g, 0.6 mmol) and the complex of tetrafluoroboric acid with diethyl ether (85%) (1.0 mL) in acetonitrile (5.0 mL) was stirred at 25°C for 1 h. Solvent removal left a residue. Reprecipitation (acetonitrile/chloroform) gave a colorless solid, 0.20 g (72%), identical with the dinitramine **9** • 2 HBF_4 • H_2O.

A similar treatment converted the tetranitroso compound **10** • 2.5 H_2O to the dinitrosamine **11** • 2 HBF_4 as a colorless solid, 0.43 g (60%).

ACKNOWLEDGMENT

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