Heteroatom Chemistry
Volume 2, Number 6, 1991

Dense Compounds of C, H, N, and O Atoms: II [1]. Nitramine and Nitrosamine Derivatives of 2-Oxo- and 2-Iminooctahydroimidazo-[4,5-*d*]imidazole

Vayalakkavoor T. Ramakrishnan, Murugappa Vedachalam, and Joseph H. Boyer*

Department of Chemistry, University of New Orleans, New Orleans, LA 70148, U.S.A.

Received 10 June 1991.

ABSTRACT

The 4,6-dinitroso derivative **11** *was obtained (83%) by the nitrosation of 2-oxooctahydroimidazo*[*4,5*-d]-*imidazole* **1** *as the dihydrochloride and was converted to the 4,6-dinitro derivative* **12** [*66%*] *by treatment with nitric acid (100%, −40°C) and to the 1,4,6-trinitro derivative* **13** *(66%) and the 1,3,4,6-tetranitro derivative* **2** *(86%) by treatment with nitric acid (100%) in acetic anhydride at 0–5°C and 10–25°C respectively. Similar treatment with nitric acid (100%) in either acetic or trifluoroacetic anhydride at 0–25°C converted the trinitro compound* **13** *to the tetranitro compound* **2** *(86%). The dinitramine* **12** *was also obtained (43%) from the diamine* **1** *by nitration with nitric acid (100%, −40°C). A reaction between 2-nitrimino-5-iminooctahydroimidazo*[*4,5*-d]*imidazole* **7** *as a hydrochloride salt (from an acid catalyzed condensation between 4,5-dihydroxy-2-nitriminoimidazolidine* **6** *and guanidine) and nitric acid (100%, −40°C) gave the 2,5-dinitrimino derivative* **14** *(85%) isolated as a monohydrate. The nitrate salt* **7** · HNO_3, *isomeric with* **14** · H_2O, *was obtained from the corresponding hydrochloride* **7** · *HCl and silver nitrate. Both nitrimines* **7** *and* **14** *gave 1,3,4,6-tetranitro-2,5-dioxooctahydroimidazo*[*4,5*-d]*imidazole* **15** *(66% and 59%) by treatment with nitric acid (100%) in acetic anhydride.*

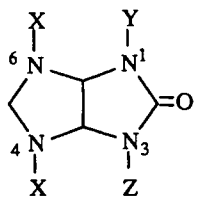
INTRODUCTION

Critical properties, for example, detonation velocity and detonation pressure, for energetic compounds derived from C, H, N, and O atoms and designed for use in formulations for explosives and propellants were generally enhanced by high density ($d \sim 2.0$) [2]. Recently the preparation of the 1,3,4,6-tetranitro derivative **2**, $d = 1.91$, by the treatment of 2-oxooctahydroimidazo[4,5-*d*]imidazole **1** with nitric acid in acetic anhydride was reported [3]. Attempts to bring about the same or related nitration of the heterocycle **2** when the nitrating agent was either nitric acid, a mixture of nitric acid and ammonium nitrate, or a mixture of nitric and sulfuric acids were unsuccessful [3].

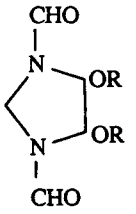
The preparation of the heterocycle **1** [3] was brought about by an acid catalyzed condensation between urea and 1,3-diformyl-4,5-dihydroxyimidazolidine **4** (an adduct from *N,N'*-diformylmethylendiamine **3** and glyoxal) (see Equation 1) [4]. In similar reactions guanidine and urea were alkylated by the cyclic amidal, 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine **5** [1, 5]. Related alkylations of urea, guanidine, and thiourea by 1,2-dicarbonyl compounds presumably required the intermediacy of cyclic bisamidals [6]. Elsewhere the versatility of α-methoxyamides in acid catalyzed nucleophilic substitution reactions was a dominant feature in an important method for α-functionalization of amides [7].

*To whom correspondence should be addressed.

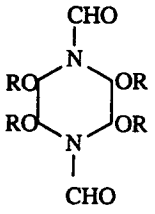
1042-7163/92/$3.50 + .25



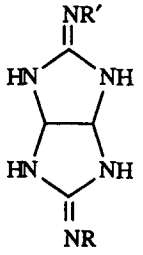
1 X = Y = Z = H
2 X = Y = Z = NO_2
11 X = NO, Y = Z = H
12 X = NO_2, Y = Z = H
13 X = Y = NO_2, Z = H



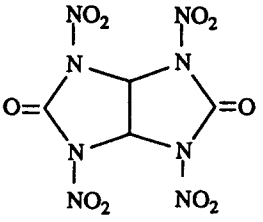
4 R = H
9 R = $COCH_3$



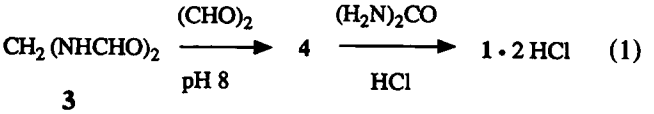
5 R = H
10 OR = Cl



7 R = H, R′ = NO_2
8 R = R′ = H
14 R = R′ = NO_2



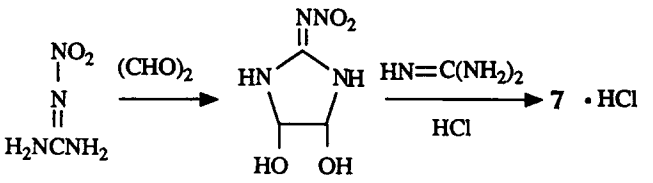
15



3 (1)

RESULTS AND DISCUSSION

A condensation with guanidine in the presence of hydrochloric acid to give 2-nitrimino-5-iminooctahydroimidazo[4,5-*d*]imidazole **7**, isolated as a hydrochloride salt (Equation 2), established 4,5-dihydroxy-2-nitriminoimidazolidine **6** (from nitroguanidine and glyoxal) [8] as a cyclic bisamidal alkylating agent. An absence of the formation of 2,5-diiminooctahydroimidazo[4,5-*d*]imidazole **8** was an indication of the resistance of the amidal **6** toward dissociation to nitroguanidine and glyoxal since the latter was known to condense with guanidine to give "glycocyamidine" **8** [6]. Exploration of nucleophilic reactions of related α-functionalized amides in the absence of an acid catalyst were unsuccessful, e.g., the diacetate ester **9** [9] of the cyclic bisamidal **4** was unreactive to the potassium salt of methylenedinitramine [$CH_2(NHNO_2)_2$], and the tetrachloro derivative **10** [10] of the cyclic bisamidal **5** was unreactive to sodium azide. A limited application of the amidal **4** as an alkylating agent was revealed when replacement of urea with the diamide **3** afforded no reaction.



6 (2)

The dihydrochloride salt **1** · 2 HCl was converted to the 4,6-dinitroso derivative **11** in a straightforward nitrosation by aqueous sodium nitrite without competition from nitrosation at urea nitrogen atoms in positions 1 and 3. Conversion of the dinitrosamine to the dinitramine **12** was brought about by treatment with nitric acid (100%) at −40°C. A differentiation between a nitration/denitrosation mechanism and a direct oxidation for the conversion was not determined; however, related conversions of certain nitrosamines to nitramines brought about by treatment with nitric acid proceeded by a displacement mechanism [11–13] whereas treatment with a peroxide effected the conversion by oxidation [14, 15]. The dinitramine **12** was less efficiently obtained directly from the diamine **1** by nitration with nitric acid (100%, −40°C). The dinitrosamine **11** was further nitrated to the 1,4,6-trinitro derivative **13** by nitric acid (100%) at 10–15°C or by nitric acid in acetic anhydride at 0–5°C, and to the 1,3,4,6-tetranitro derivative **2** by nitric acid (100%) in acetic anhydride at 15–25°C. Similar treatment converted the trinitramine **13** to the tetranitramine **2**.

Nitric acid (100%) at −40°C converted the heterocycle **7** to the 2,5-dinitrimino derivative **14**, an assigned structure supported by spectroscopic and elemental analyses and in agreement with the generalization that *N*-nitroguanidines are nitrimines rather than nitramines [16, 17]. Attempts to convert the bisguanidine **7** to a derivative with a di- or trinitroguanidino moiety were unsuccessful. Both heterocycles **7** and **14** were converted to the energetic compound Sorguyl **15**, d = 2.02 [18–20], on treatment with nitric acid (100%) in acetic anhydride.

EXPERIMENTAL

Instruments included a Pye-Unicam PS 200 IR spectrophotometer, a Varian EM 360 A and Joel FX 90 Q spectrometers. Elemental analyses were obtained from Midwest Microlab, Indianapolis, IN, and Galbraith Laboratories, Knoxville, TN. A program for the calculation of the density and other properties of C, H, N, and O compounds was obtained from the Naval Weapons Center, China Lake, CA. All nitrosamines and nitramines are potentially explosive and should be handled as hazardous material. Preparative *N*-nitrations should be carried out cautiously behind a protective shield in a well-ventilated hood.

2-Oxooctahydroimidazo[*4,5*-d]*imidazole* **1**

Methylenediformamide (**3**) prepared from formamide and hexamethylenetetramine [21] was treated with glyoxal to give 1,3-diformyl-4,5-dihydroxyimidazolidine (**4**) mp 146–8°C (dec) [lit. mp 144–5°C (dec)] [22]. To a solution of urea (3.5 g, 0.6 mol) in concentrated hydrochloric acid (14 mL), cooled to 10–15°C, the imidazolidine **4** (8.0 g, 0.05 mol) was added in portions and the mixture was stirred for 2 h. A light yellow precipitate was removed, washed with absolute ethanol, and dried to isolate the diamine **1** as the dihydrochloride, 4.0 g, (40%) mp 160°C (slow decomposition with darkening) (lit. mp 159°C) [3], IR (KBr): ν 1710. Attempts to liberate the free base **1**, calcd. *d* 1.57, from its hydrochloride salt were unsuccessful.

4,6-Dinitroso-2-oxooctahydroimidazo-[*4,5*-d]*imidazole* **11**

To a solution of sodium nitrite (4.0 g) in water (10 mL) cooled to 0°C a solution of the dihydrochloride of the diamine **1** (0.8 g, 4.0 mmol) in water (8 mL) was added dropwise. A solid separated instantaneously and was removed from the mixture after stirring for 2 h and washed with water to isolate the dinitrosamine **11** (0.62 g, 83.3%), mp 215°C (explosive dec) (ethylacetate-dimethyl sulfoxide). IR (KBr): ν 3240, 3130, 1740, 1690, 1425; ^{1}H NMR (DMSO-d_6): δ 8.5 (s, NH), 6.85 (s, CH), 5.55 and 4.9 (AB q, J = 13 Hz, CH_2) and 8.4 to 4.9 (complex signals); ^{13}C NMR: δ 159.48, 70.85, 70.45, 65.19, 60.31, 58.10. Anal. Calcd. for $C_4H_6N_6O_3$: C, 25.80; H, 3.22; N, 45.16. Found: C, 25.84; H, 3.31; N, 44.89. Calcd. *d* 1.70.

4,6-Dinitro-2-oxooctahydroimidazo-[*4,5*-d]*imidazole* **12**

The dinitrosoamine **11** (0.9 g, 5.0 mmol) was slowly added to nitric acid (100%, 5 mL) at −45°C. The reaction mixture was stirred for 15 min and poured over crushed ice. The aqueous solution was extracted with ethyl acetate (3 × 25 mL), washed with saturated aqueous sodium chloride (2 × 20 mL), and dried over magnesium sulfate. Ethyl acetate was removed under vacuum to leave the dinitramine **12** as a colorless solid (0.7 g, 66%) mp: 231°C (dec) from acetone. IR (KBr): ν 3370, 3210, 1715, 1540, 1505, 1395, 1380, 1300; ^{1}H NMR (DMSO-d_6): δ 8.25 (s, 2 H NH), 6.13 (s, 2 H, CH) 5.7 and 5.5 (AB q, 2 H, J = 8 Hz, CH_2); ^{13}C NMR: δ 159.7, 72.3, 63.6. Anal. Calcd. for $C_4H_6N_6O_5$: C, 22.01; H, 2.75; N, 38.53. Found: C, 22.05; H, 2.76; N, 37.73. Calcd. *d* 1.86.

The dihydrochloride of the diamine **1** (1.0 g, 5.0 mmol) was added in small portions to nitric acid (100%) (10 mL) at −40°C with stirring. After stirring for 1 h at the same temperature it was poured onto crushed ice. A solid was isolated and washed with water to leave the dinitramine **12** (0.5 g, 43%).

1,4,6-Trinitro-2-oxooctahydroimidazo-[*4,5*-d]*imidazole* **13**

The dinitrosamine **11** (0.5 g, 2.7 mmol) was added in small portions to nitric acid (100%) (3 mL) at 0°C. Acetic anhydride (3 mL) was added dropwise and the mixture was stirred for 2 h at 0–5°C as a colorless solid separated. It was isolated and washed with cold water to give the trinitro compound **13** (0.47 g, 66%), mp 200°C (explosive dec) (ethyl acetate-dimethyl sulfoxide). IR (KBr): ν 3230, 3170, 1790, 1580, 1530, 1380, 1280; ^{1}H NMR (DMSO-d_6): δ 9.9 (s, NH), 7.4 and 6.1 (AB q, 2 H, J = 7.5 Hz, CH), 6.2 and 5.5 (AB q, 2 H, J = 11 Hz, CH_2); ^{13}C NMR: δ 148.49, 74.88, 67.33, 64.67. Anal. Calcd. for $C_4H_5N_7O_7$: C, 18.25; H, 1.90; N, 37.26. Found: C, 18.23; H, 1.73; N, 36.75. Treatment of the nitrosamine **11** (0.93 g, 5.0 mmol) with nitric acid (100%) (7 mL) at 0°C for 0.5 h then at 10–15°C for 1.5 h gave the trinitro compound **13** (67%). Calcd. *d* 1.93.

2,4,6,8-Tetranitro-2-oxooctahydroimidazo-[*4,5*-d]*imidazole* **2**

The dinitrosamine **11** (1.5 g, 8.0 mmol) was added in small portions to nitric acid (100%) at 0°C. Acetic anhydride (10 mL) was added and the reaction mixture was stirred at 10–15°C for 1 h then at room temperature for 2 h. The tetranitro compound **2** (1.7 g, 68.5%) was isolated after trituration with cold water, mp 215°C (explosive dec) lit. [3] mp 212°C (dec). IR (KBr): ν 1805, 1580, 1310, 1255; ^{1}H NMR (DMSO-d_6): δ 7.3 (s, 2 H, CH), 6.8 and 5.5 (AB q, 2 H, J = 13 Hz, CH_2); ^{13}C NMR: δ 140.62, 72.41, 64.61. Calcd. *d* 1.99, experimental *d* 1.91 [3].

The tetranitro compound **2** was also obtained in 86% yield from the trinitro compound **13** on treatment with nitric acid (100%) and either acetic anhydride or trifluoroacetic anhydride at 0°C followed by stirring at 25°C for 20 h.

2-Nitrimino-5-Iminooctahydroimidazo-[*4,5*-d]*imidazole* **7**

To a stirred solution of guanidine hydrochloride (5.6 g, 0.06 mol) in concentrated hydrochloric acid (12 mL) 4,5-dihydroxy-2-nitriminoimidazolidine **6** [8] (4 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 absolute alcohol (3 × 10 mL), reprecipitated (dimethyl sulfoxide/chloroform), and dried to give the nitroguanidine **7** as the monohydrochloride derivative, 1.85 g, (36%), mp 268– 270° (explosive dec), IR (KBr): ν 3330, 3160–3080, 1680, 1575, 1465, 1270, 1120, 1095, 880; ^{1}H NMR (DMSO-d_6): δ 5.68 (s, 2 H, CH), 8.10 (s, 2 H), 9.00 (s, 2 H), 9.28 (s, 2 H) for NH

and NH_2^+; ^{13}C NMR (DMSO-d_6): δ 160.98, 158.83, 69.48. Anal. Calcd. for $C_4H_8N_7O_2Cl$: C, 21.68; H, 3.61; N, 44.25; Cl, 16.01. Found: C, 21.40; H, 3.58; N, 41.44; Cl, 12.00. Attempts to liberate the free base **7**, calcd. *d* 1.69, from its hydrochloride salt were unsuccessful.

To a solution of the hydrochloride of the nitrimine **7** (0.5 g, 2.3 mmol) in distilled water (3 mL) silver nitrate (0.4 g, 2.3 mmol) solution in distilled water (2 mL) was added. The reaction mixture was stirred for 10 min and silver chloride was isolated and washed with distilled water (2 mL). The combined filtrate was evaporated to one tenth of its original volume and absolute alcohol (3 mL) was added. A solid was isolated and washed with distilled water (1 mL) and absolute alcohol (2 mL) and dried to give the salt **7** · HNO_3 (0.2 g, 35%). mp 245–246°C (explosive dec). IR (KBr): 3368–3183, 1701, 1575, 1456, 1304, 1294, 1249, 1084, 890, 637 cm^{-1}; ^1H NMR (DMSO-d_6): δ 5.73 (s, 2H, CH), 7.98 (bs, 2H), 9.03 (bs, 2H), 9.42, (bs, 2H) for NH and NH_2^+; ^{13}C NMR (DMSO-d_6): δ 161.24, 158.83, 69.80. Anal. Calcd. for $C_4H_8N_8O_5$: C, 19.35; H, 3.23; N, 45.16. Found: C, 19.28; H, 3.18; N, 44.86. Calcd. *d* 1.82.

2,5-Dinitriminooctahydroimidazo-[4,5-d]imidazole **14**

The guanidine **7** as a hydrochloride (1.5 g, 7.2 mmol) was added in portions to a stirred solution of nitric acid (100%) (20 mL) at −40°C. Stirring was continued for 1 h and the mixture was poured over ice. A solid separated on standing (1 h) and was isolated and washed with ice-cold water. The colorless powder was dissolved in dimethyl sulfoxide and reprecipitated with chloroform to give the dinitrimine **14** as a monohydrate (1.4 g, 84%), mp 243–245°C (explosive dec). IR (KBr): ν 3390, 3320, 3200, 1690, 1575, 1285, 1240, 1095, 885; ^1H NMR (DMSO-d_6): δ 5.84 (s, 2H, CH), 8.05 (bs, 2 H), 9.07 (bs, 2 H), and 9.49 (bs, 2H) for NH and H_2O; ^{13}C NMR (DMSO-d_6): δ 161.17, 158.90, 69.94. Anal. Calcd. for $C_4H_8N_8O_5$: C, 19.35; H, 3.23; N, 45.16. Found: C, 19.72; H, 3.28; N, 41.48. The bisguanidine **14**, calcd. *d* 1.76, was not liberated from its hydrate.

2,5-Dioxo-1,3,4,6-tetranitrooctahydro-imidazo[4,5-d]imidazole **15** *(Sorguyl)*

(a) To a solution of nitric acid (100%) (10 mL) the nitroguanidine **7** as a hydrochloride (1 g, 4 mmol) was added with stirring in small portions at 0°C. The mixture was stirred for 15 min, acetic anhydride (10 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 isolated, washed with ice water (3 × 10 mL), and dried to give the tetranitrourea **15** (Sorguyl) (0.96 g, 66%) as a colorless solid, mp 132°C (explosive dec) [lit. [18] explosion temperature 133°C and mp ca. 225°C (dec), lit. [19] dec 200°C, and lit. [20] mp 241°C); IR (KBr): ν 2999, 1825, 1801, 1626, 1587, 1300, 1250, 1097, 812, 744, 700; ^1H NMR (acetone-d_6): δ 7.70 (s); Anal. Calcd. for $C_4H_2N_8O_{10}$: C, 14.91; H, 0.62; N, 34.78. Found: C, 15.07; H, 0.54; N, 31.44. (b) The dinitroguanidine **14** as a monohydrate (1.0 g, 4 mmol) was added in small portions at 0°C with stirring to nitric acid (100%) (10 mL). The mixture was stirred for 15 min, acetic anhydride (10 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 filtered, washed with chloroform (3 × 10 mL) and dried to give the tetranitrourea **15**, 0.77 g (59%), mp 132°C (explosive dec). Calcd. *d* 2.07, experimental *d* 2.02 [18–20].

ACKNOWLEDGMENT

Financial support was received from ONR.

REFERENCES

[1] Part I: M. Vedachalam, V. T. Ramakrishnan, J. H. Boyer, *Het. Chem.*, 1991, 313.
[2] S. Iyer, N. Slagg; Molecular Aspects in Energetic Materials, in J. F. Liebman, A. Greenberg (eds.), *Structure and Reactivity*, VCH Publishers, New York, p. 274 (1988).
[3] L. Wenjie, H. Guifen, C. Miahong, *Proceedings of the International Symposium on Pyrotechnics and Explosives*, Beijing, China, p. 187 (1987).
[4] S. L. Vail, C. M. Morgan, H. B. Moore, *J. Org. Chem., 27*, 1962, 2067.
[5] M. Vedachalam, V. T. Ramakrishnan, J. H. Boyer, I. J. Daigley, K. A. Nelson, H. G. Adolph, R. Gilardi, C. George, J. L. Flippen-Anderson, *J. Org. Chem., 56*, 1991, 3413.
[6] C. Lempert, *Chem. Rev., 59*, 1959, 667, 685.
[7] P. D. Palasz, J. H. P. Utley, *J. Chem. Soc., Perkin Trans. II*, 1984, 807.
[8] A. H. Dinwoodie, J. M. C. Thomson, Brit. 1,103,285 (1968); *Chem. Abstr, 69*, 3614k (1968).
[9] W. M. Koppes, M. Chaykovsky, H. G. Adolph, R. Gilardi, C. George, *J. Org. Chem., 52*, 1987, 113.
[10] A. C. Currie, A. H. Dinwoodie, G. Fort, J. M. C. Thompson, *J. Chem. Soc. (C)*, 1967, 491.
[11] G. Kumar, V. T. Ramakrishnan, J. H. Boyer, Heterocycles, *29*, 1989, 1997.
[12] G. A. Sokol'skii, S. S. Dubov, A. N. Medvedev, L. I. Ragulin, F. N. Chelobov, Yu. M. Shalaginov, I. L. Knunyants, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1972, 129; Engl. transl., p. 116.
[13] R. F. Gafurov, A. G. Korepin, E. M. Sogomonyan, A. N. Salakhova, L. T. Eremenko, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1972, 1876; Engl. transl., p. 1823.
[14] H. Feuer, A. T. Nielsen: *Nitro Compounds. Recent Advances in Synthesis and Chemistry*, VCH Publishers, New York, p. 499. (1990).

[15] R. G. Gafurov, E. M. Sogomonyan, L. T. Eremenko, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1971, 2606; Eng. transl. p. 2480.
[16] L. T. Davis, K. C. Blanchard, *J. Amer. Chem. Soc., 51*, 1929, 1790, 1801.
[17] G. A. Olah, R. Malhotra, S. C. Narang: *Nitration Methods and Mechanism*, VCH Publishers, New York, p. 277. (1989).
[18] *Encyclopedia of Explosives and Related Items, Vol. 1–10*, ARDEC, Dover, New Jersey, 1974, *6*, G117. The encyclopedia is available from National Technical Information and Service, Springfield, VA 22151.
[19] J. Boileau, J. M. L. Emery, J. P. A. Kehren, Ger. Offen. 1975, No. 2435651; *Chem. Abstr., 83*, 1975, 30483r.
[20] Y. Zheng, J. Zhou, D. Zhou, M. Zhang, *Binggong Xuebao*, 1988, 59; *Chem. Abstr., 109*, 1988, 189782q.
[21] C. W. Sauer, R. J. Bruni, *J. Am. Chem. Soc., 77*, 1955, 2559.
[22] S. L. Vail, C. M. Moran, H. B. Moore, R. M. H. Kullman, *J. Org. Chem., 27*, 1962, 2071.