Dense Compounds of C, H, N, and O Atoms. II. Nitramine and Nitrosamine Derivatives of 2–Oxo–
and 2–Iminoctahydroimidazo[4,5–d]imidazole

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**Title:** Dense Compounds of C, H, N, and O Atoms. II. Nitramine and Nitro-samine Derivatives of 2-Oxo- and 2, -Iminoctahydroimidazo 4,5-d imidazole

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**Abstract:** See Attached Report

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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- imino octahydroimidazo[4,5-d]imidazole 7 as a hydrochloride salt (from an acid catalysed condensation between 4,5-dihydroxy-2-nitriminimidazolidine 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 • HNO₃, isomeric with 14 • H₂O, 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, e.g., 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 ~ 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 nitrations of the heterocycle 2 when the nitrating agent was either nitric acid, or 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 catalysed condensation between urea and 1,3-diformyl-4,5-dihydroxymidazolidine 4 (an adduct from N,N'-diformylmethylendiamine 3 and glyoxal), eq(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].

![Chemical structures](image)

1  X = Y = Z = H
2  X = Y = Z = NO₂
11 X = NO, Y = Z = H
12 X = NO₂, Y = Z = H
13 X = Y = NO₂, Z = H

4  R = H
9  R = COCH₃
RESULTS AND DISCUSSION

A condensation with guanidine in the presence of hydrochloric acid to give 2-nitrimino-5-iminooctahydroidazol[4,5-d]imidazole 7, isolated as a hydrochloride salt, eq(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 [CH₂(NHNO₂)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.
The dihydrochloride salt $1 \cdot 2 \text{HCl}$ 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 $-40^\circ \text{C}$. 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%, $-40^\circ \text{C}$). The dinitrosamine $11$ was further nitrated to the 1,4,6-trinitro derivative $13$ by nitric acid (100%) at $10 - 15^\circ \text{C}$ or by nitric acid in acetic anhydride at $0 - 5^\circ \text{C}$, and to the 1,3,4,6-tetranitro derivative $2$ by nitric acid (100%) in acetic anhydride at $15 - 25^\circ \text{C}$. Similar treatment converted the trinitramine $13$ to the tetranitramine $2$.

Nitric acid (100%) at $-40^\circ \text{C}$ 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 tri-nitroguanidino 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.

2-Oxo octahydroimidazo[4,5-d]imidazole 1. Methyleneformamide (3) prepared from formamide and hexamethylenetetramine, [21] was treated with glyoxal to give 1,3-diformyl-4,5-dihydroximidazolidine (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; 1H NMR (DMSO- d6): δ 8.5 (s, NH), 6.85 (s, CH), 5.55 and 4.9 (AB q, J = 13 Hz, CH2) and 8.4 to 4.9 (complex signals); 13C NMR: δ 159.48, 70.85, 70.45, 65.19, 60.31, 58.10. Anal. calcld for C4H6N6O3: 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 x 25 ml), washed with saturated aqueous sodium chloride (2 x 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, 1395, 1380, 1300; 1H NMR (DMSO-d6): 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, CH2); 13C NMR: δ 159.7, 72.3, 63.6. Anal. calcd for C4H6N2O5: 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 hr 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; 1H NMR (DMSO-d6): 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, CH2); 13C NMR: δ 148.49, 74.88, 67.33, 64.67. Anal. calcd for C4H5N7O7: C, 22.25; 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): υ 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 x 10 ml), reprecipitated (dimethyl sulfoxide/chloroform), and dried to give the nitroguanidine 7 as the monohydrochloride derivative, 1.85 g, (36%), mp 268-270 °C (explosive dec); IR (KBr): υ 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 NI-I and NT“I<; $^{13}$C NMR (DMSO–d$_6$): δ 160.98, 158.83, 69.48. Anal. calcd for C$_4$H$_8$N$_7$O$_2$Cl: 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$^{-1}$; $^1$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-$d_6$): $\delta$ 161.24, 158.83, 69.80.

Anal. calcd for C$_4$H$_8$N$_8$O$_5$: 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-Dinitrimino-octahydroimidazo[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 $-40^\circ$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): $\nu$ 3390, 3320, 3200, 1690, 1575, 1285, 1240, 1095, 885; $^1$H NMR (DMSO-$d_6$): $\delta$ 5.84 (s, 2 H, CH), 8.05 (bs, 2 H), 9.07 (bs, 2 H), and 9.49 (bs, 2 H) for NH and H$_2$O; $^{13}$C NMR (DMSO-$d_6$): $\delta$ 161.17, 158.90, 69.94. Anal. calcd for C$_4$H$_8$N$_8$O$_5$: 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-tetranitro-octahydroimidazo[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 x 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): $\nu$ 2999, 1825, 1801, 1626, 1587, 1300, 1250, 1097, 812, 744, 700; $^1$H NMR (acetone-$d_6$): $\delta$ 7.70 (s); Anal. calcd for C$_4$H$_2$N$_8$O$_{10}$: 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 pre-
Cipitate was filtered, washed with chloroform (3 x 10 ml) and dried to give the tetranitro-
urea 15, 0.77 g (59%), mp 132 °C (explosive dec). Calcd d 2.07, experimental d 2.02 [18 -
20].

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