

TETRAHEDRON

# Synthesis and Reactions of 1,1-Diamino-2,2-dinitroethylene

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Abstract: Low temperature nitrations of 2-methylimidazole gave in addition to the known 2-methyl-5(4)-nitroimidazole (1), 2-(dinitromethylene)-5,5-dinitro-4-imidazolidinone (3) and parabanic acid (2). The tetranitro compound 3 was also obtained by nitration of 2-methyl-4,5-dihydro-(1H)-5-imidazolone (8). Thermal decomposition of 3 gave 2-(dinitromethylene)-4,5imidazolidinedione (4) which also was the product from nitration of the new compound 2-methoxy-2-methyl-4,5imidazolidinedione. Treatment of 4 with aqueous ammonia gave the previously unknown 1,1-diamino-2,2-dinitroethylene (5). The physical properties and chemical behaviour of (5) are described. © 1998 Published by Elsevier Science Ltd. All rights reserved.

There is a need for new energetic compounds with combined high efficiency and low sensitivity<sup>1</sup>. Accordingly several new explosives such as 3-nitro-1,2,4-triazolin-5-one (NTO)<sup>2</sup> and some nitroimidazoles have been investigated. Examples of the last mentioned type compounds include 2,4,5-trinitroimidazole, 3-methyl-5-nitro-2(1H)-imidazolone (as an analogue to NTO)<sup>3,4</sup> and nitrated di-imidazoles<sup>5</sup>. Also for this purpose a series of 1,1-bisalkylamino-2,2-dinitroethylenes that has been synthesised by Baum and co-workers by reaction of 1,1-diiodo-2,2-dinitroethylenes with amines<sup>6</sup>.

However attempts to obtain the most interesting substance in this series, namely 1,1-diamino-2,2-dinitroethylene itself, failed. In our approach to 1,1-diamino-2,2-dinitroethylene we used another methodology including hydrolytic cleavage of nitrated heterocycles. A similar approach has been used previously for the synthesis of 1,1-diamino-2-cyano-2-nitroethylenes<sup>7</sup>, and nitration of 2-methylimidazole was chosen as a possible route to the target molecule.

Nitroimidazoles have been extensively studied<sup>8,9</sup> and reviewed<sup>10</sup>. Kinetic studies and preparative experiments clearly indicate that there are alternative reaction pathways in the nitration of both imidazole and 2-methylimidazole. These previous results indicated a number of products, of which only 4(5)-mononitro- and 4,5dinitroimidazoles (**1a-d**) have been definitely characterised, and products from reaction conditions that mainly led to destruction of the imidazole ring were not analysed<sup>11-12</sup>.



Our preliminary experiments confirmed that the yields of 2-methyl-4(5)nitroimidazole in such high temperature nitrations of 2-methylimidazole were far from quantitative. The strong and characteristic UV absorption of the aqueous phase indicated the presence of substantial amounts of polynitroaliphatic anions. For this reason most attention in this work was focused on low temperature nitration of 2methylimidazole in an attempt to isolate intermediates prior to ring cleavage. Nitration of 2-methylimidazole by nitric acid in 85-105 % sulfuric acid was found to proceed rather fast at ambient temperature with reaction times varying from 3 to 6 h, which is consistent with data for imidazole itself<sup>12</sup>. The product pattern was strongly dependent on the acid concentration.

Nitric acid in 101-105 % sulfuric acid at 15-25 °C gave mainly 2-methyl-4(5)nitroimidazole in 50-70 % yield together with some parabanic acid (2), which was isolated after aqueous work-up as the relatively insoluble ammonium salt. Nitration in 80-100 % sulfuric acid at the same temperature changed the outcome completely and a previously unobserved unstable intermediate with the supposed structure 3 was isolated as a solid in modest yields (15 % optimum in 9 2% H<sub>2</sub>SO<sub>4</sub> at 15-18 °C). The major product formed was parabanic acid (60 % yield under optimal conditions) and small amounts of 2-methyl-4(5)-nitroimidazole (1). Compound 3 proved to be thermally unstable at ambient temperature. It decomposes into 2-(dinitromethylene)-4,5imidazolidinedione (4) in approximately 5 hours losing nitrogen oxides. The amount of oxides evolved (26.5 %) is very close to the theoretical figure(27.3 %) that corresponds to the loss of N<sub>2</sub>O<sub>3</sub> from 3 to form 4. In solution this decomposition was considerably more rapid, and no reliable spectral data could be obtained of this highly unstable explosive compound. All attempts to record e.g. the <sup>13</sup>C NMR spectrum gave the three signals (157.7, 149.4, 130.1) characteristic for the dione 4. Attempts to produce KBr disks of 3 are not recommended because evolution of  $NO_x$  will occur. Compound 4, on the other hand, was found to be thermally stable, which allowed its characterisation ... The assignment of structure 3 was based on the comparison of its behaviour with the previously observed decomposition of 3,3,5,7-tetranitrooxindole to 5,7-dinitroisatin<sup>13</sup> and on the amount of nitrogen oxides evolved in its decomposition to 4.



According to  ${}^{13}$ C NMR studies 4 undergoes slow decomposition in DMSO yielding finally parabanic acid (2).

Addition of either compound 3 or 4 to water and neutralisation by aqueous ammonia to pH 8-9 resulted in quick dissolution and formation of the ring cleavage products ammonium oxalate and the insoluble 1,1-diamino-2,2-dinitroethylene (5) (Scheme 1).

Although a number of substituted derivatives of 5, such as 6, previously have

been prepared by displacement reactions (using secondary amines) of 1,1-diiodo-2,2dinitroethylene, this method failed when ammonia was used as reactant. In this case the sole product was ammonium cyanodinitromethide,  $NH_4C(NO_2)CN$ , presumably formed by loss of HI from the monosubstituted intermediate, i.e. 1-amino-1-iodo-2,2-dinitroethylene<sup>6</sup>.





1,1-Diamino-2,2-dinitroethylene (5), now reported for the first time, is a stable compound. Its properties are similar to amidinoformic acid<sup>14</sup>. Both compounds are strongly dipolar and have similar infrared absorption corresponding to a protonated amidine function. Both compounds are very weak bases and can only be dissolved in strong acids. Compound 5 is also very poorly soluble in common organic solvents and water, but can readily be dissolved in solvents like DMSO and DMF. It is quite stable thermally and on heating it decomposes in two separate exothermic steps at 220 °C and 275 °C. The structure of this compound was finally confirmed by a single crystal X-ray study.

Single-crystal X-ray diffraction studies of 1,1-diamino-2,2-dinitroethylene (5) showed that the molecule in the crystal structure has bond lengths and bond angles as expected for this type of push-pull ethylenes<sup>6</sup>. The bond distances found in the structure are a lengthened ethylene bond distance of 1.45(1) Å, two amino N-C bond distances of 1.31(1) Å and 1.32(1) Å respectively and two nitro N-C bond distances of 1.42(1) Å and 1.39(1) Å, respectively. Two short intramolecular hydrogen bonds between the nitro oxygen atoms and the amino hydrogen atoms are present. The two carbon atoms and the four nitrogen atoms in the molecule are nonplanar with a twist of ~6 ° for the nitro nitrogen atoms. The observed geometry of the molecule indicates extensive  $\pi$ -conjugation present. The molecular packing is built up by two-dimensional infinite

wave shaped layers, with extensive intermolecular hydrogen bonding within the layers and Van der Waals interactions between the layers. The crystal packing explains some of the physical properties such as the absence of a melting point and the low solubility of the compound. The details of the single crystal X-ray diffraction studies of 1,1-diamino-2,2-dinitroethylene have been submitted for publication<sup>15</sup>.

Compound 5 has the properties of a high explosive with a performance close to that of the common high explosive RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) but with lower sensitivity to impact and friction. A comparison of sensitivity and detonation data of 5 and RDX is presented in Table 1. It might be added that the regio isomers of 5, *cis-* and *trans-*1,2-diamino-1,2-dinitroethylenes are still unknown compounds, although other 1,2-dinitroethylenes are known, such as *trans-*1,2-difluoro-1,2-dinitroethylene<sup>16</sup>.

Table 1. Comparison of RDX and 1,1-Diamino-2,2-dinitroethylene.

	RDX	1,1-Diamino-2,2- dinitroethylene
Dropweight test (cm)	38	126
Friction test (N)	120	>350
Detonation Pressure* (GPa)	34.63	33.96
Detonation Velocity* (m/s)	8869	8930

\*Calculated using Cheetah 1.4 and BKWC equation of state. Heat of formation used in the calculations was -32 kcal/mole (experimental).

The nucleophilicity of the <u>gem</u>-diamino functionality in 5 is extremely low. No reaction with 1,2-dibromoethane was observed even in hot DMF. But under basic conditions 6 could be obtained in high yield. Compound 6 was spectroscopically identical with the product previously prepared from ethylenediamine and 1,1-diiodo-2,2-dinitroethylene<sup>6</sup>.

Reaction between 5 and oxalyl chloride in acetonitrile at reflux gave the 4,5imidazolidinedione (4) previously obtained by decomposition of 3. In a related experiment of interest, 1,1-diamino-2,2-dimethoxycarbonylethylene reacted with oxalyl chloride to give 7 in a high yield<sup>17</sup>.



From the available experimental data it is hard to judge about the mechanism of the formation of the tetranitro compound 3. However, it was shown in a separate experiment that 2-methyl-4(5)-nitroimidazole is unreactive under the reaction conditions used. This indicates that 1 is not an intermediate in the formation of 3. Hence, initial oxygenation of 2-methylimidazole to 2-methyl-4,5-dihydro-(1H)-5imidazolone  $(8)^{23}$  followed by gem-dinitration of the ring, similar to that in the nitration of oxindole<sup>12</sup> seems likely. The mechanistic assumption as to the participation of the keto functionality in the gem nitration of the endocyclic carbon was confirmed by an experiment involving nitration of 2-methyl-4,5-dihydro(1H)-5-imidazolone (8) which under the same reaction conditions as for 2-methylimidazole quickly gave a compound that in all respects behaved as the previous described 3. The electron withdrawing effect of the keto- and nitro groups probably causes polarisation of the C-H bonds in the methyl group and makes the carbon atom liable to electrophilic attack enabling the formation of **3**. Examples of such nitrations of aliphatic hydrocarbons containing acidic hydrogens can be found in the literature<sup>18-20</sup>. In addition, electrophilic attack at the methyl group in 2-methyl-4(5)-nitroimidazoles have several precedents<sup>21</sup>.

The influence of electronegative substituents in the imidazole ring on the reactivity of the methyl group in the 2-position towards electrophiles was finally demonstrated by nitration of 2-methoxy-2-methyl-4,5-imidazolidinedione (10) which readily gave compound 4 with yields up to 70 %.

The purported compound 9 was for the first time erroneously mentioned in Beilstein but the substance described in the original work<sup>22</sup> is in fact 2-methyl-4,5-dihydro-1H-4,5-imidazoledicarboxylic acid.

2-Methyl-4,5-imidazoledione was synthesised from acetamidine hydrochloride and diethyl oxalate in methanol at ambient temperature. The desired compound 9 was obtained as a mixture with 2-methoxy-2-methyl-4,5-imidazolidinedione (10) and recrystallisation of this mixture from methanol finally led to pure 10 (Scheme 2).



Scheme 2



Nitration of either the mixture or the recrystallised product gave the same yields of 4. This is explained by the formation of the same charged intermediate from 9 and 10 in sulfuric acid (Scheme 3).

#### Conclusions

We have discovered a new type of nitration in the imidazole series, namely nitrative attack of endo- and exo-cyclic carbon hydrogen bonds, leading to <u>gem</u>-dinitrocompounds (3 and 4). This work and the results of previous studies in the oxindole series indicate that such nitrations might be extended to several other heterocycles. 1,1-Diamino-2,2-dinitroethylene has interesting properties as a high explosive and might also have applications in the synthesis of nitrogen heterocycles.

# **Experimental Section**

NMR spectra were obtained using a Varian 200 MHz spectrometer. Infrared spectra were recorded with a Mattson 1000 FTIR spectrophotometer. Melting points and decomposition temperatures were determined with a Mettler DSC 30. Mass spectra were recorded with a Jeol D300. Elemental analyses were carried out by H Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. The friction sensitivity was measured with a Julius Peter friction testing apparatus. Heat of formation was obtained using a IKA-Calorimeter C 4000 adiabatic.

**Caution**; All polynitro compounds described in this paper are explosives and proper shielding is strongly recommended.

#### Nitration of 2-methylimidazole. Ammonium salt of parabanic acid (2).

Finely ground 2-methylimidazole (4.1 g, 0.050 mol) was dissolved in sulfuric acid (40 ml, 1.84 g/cm<sup>3</sup>) at 45-50°C with vigorous stirring. At the same temperature nitric acid (12.5 ml, 1.52 g/cm<sup>3</sup>) was added over a 30 min period. After 3 h at ambient temperature the reaction mixture was diluted with water (1.5 times by weight). Neutralisation with 25 % ammonia solution to pH 5-6 gave a precipitate of 2-methyl-5-nitroimidazole (0.5 g). Further adjustment of the pH to 9-11 cooling it to 10 °C and keeping it overnight resulted in the precipitation of 4.5 g (60 %) of the ammonium salt of parabanic acid (as a monohydrate).

# Nitration of 2-methylimidazole. Formation of 2-(dinitromethylene)-5,5-dinitro-4imidazolidinedione (3), 2-(Dinitromethylene)-4,5-imidazolidinedione (4) and the ammonium salt of parabanic acid (2).

Finely ground 2-methylimidazole (4.1 g, 0.050 mol) was dissolved in sulfuric acid (92 % 40 ml) at 15-20 °C with vigorous stirring. At the same temperature nitric acid (8.0 ml, 1.52 g/cm<sup>3</sup>) was added over a 30min period. In the beginning of the addition the reaction mixture became dark and then slowly turned more bright with a distinct pink coloration. After 3 hours a white precipitate of **3** was formed, which was collected and washed several times with cold trifluoroacetic acid. The precipitate was dried in vacuum at 0°C. On standing at room temperature for 5 h, 2-(dinitromethylene)-5,5-dinitro-4-imidazolidinedione lost 26.5 % of weight and gave 1.7 g (15 %) of 2-(dinitromethylene)-4,5-imidazolidinedione, **4**. Decomposition temp 240 °C (10 °C/min DSC): IR(KBr) 3305 (NH), 3280 (NH), 1805 (C=O), 1587 (NO<sub>2</sub>), 1511, 1312 NO<sub>2</sub>), 1274, 912, 807, cm<sup>-1</sup>:<sup>1</sup>H NMR(DMSO-d<sub>6</sub>)  $\delta$  11.01 ppm; <sup>13</sup>C NMR (DMSO-d<sub>6</sub>)  $\delta$  131.1, 153.5, 159.8. ppm; MS *m/e* 202 (M<sup>+</sup>): Anal. Calcd. for C<sub>4</sub>H<sub>2</sub>N<sub>4</sub>O<sub>6</sub>: C, 23.77; H, 1.0; N, 27.72. Found: C, 23.88; H, 1.25; N, 27.82.

The filtrate was diluted with water (1.5 times by weight). Neutralisation with 25 % ammonia solution to pH 5-6 gave a precipitate of 2-methyl-5-nitroimidazole (0.5 g). Further adjustment of the pH to 9-11, cooling to 10 °C and keeping over night resulted in the precipitation of 1.5 g (20 %) of the ammonium salt of parabanic acid (as a monohydrate).

#### 2-Methyl-4,5-dihydro-1H-5-imidazolone (8)

This compound was prepared by condensation of ethyl acetimidate and ethyl aminoacetate according to literature<sup>23, 24</sup>. Yield; 55 % (lit.<sup>23</sup> 64 %). mp 171-172 °C (lit. 140 °C<sup>23, 24</sup>) after recrystallisation from pyridine<sup>23</sup>. <sup>13</sup>C and <sup>1</sup>H NMR spectra were in agreement with the lit.<sup>24</sup>. The reason for the discrepancy of the melting points is not clear but might be due to various tautomers in the solid state.

#### Independent synthesis of 3

2-Methyl-4,5-dihydro-1*H*-5-imidazolone (8) (0.98 g, 10 mmol) was added in portions to a solution of nitric acid (2.0 ml) in sulfuric acid (9.0 ml) at 0-5 °C. The clear solution was allowed to reach 15 °C during 1 hour and stirred at this temperature for an additional hour. During this period the product separated as a solid, which was collected by filtration after dilution of the reaction mixture with trifluoroacetic acid (6 ml) and cooling to 5 °C. The precipitate was washed with trifluoroacetic acid, dried and stored in a refrigerator. Yield; 0.75 g (27 %).

#### **Independent synthesis of 4**

1,1-Diamino-2,2-dinitroethylene (148 mg, 1.00 mmol) was added to acetonitrile (6.0 ml) at 25 °C. Oxalyl chloride (190 mg, 1.5 mmol) was added to the stirred mixture, which was then kept under reflux for 2 min to give a clear solution and evolution of HCl. Concentration of the solution to ca 3 ml followed by addition of diisopropyl ether gave the product as a white solid, which was recrystallised from toluene/acetonitrile. Yield: 170 mg (83 %). The IR and mass data were identical with those for the product obtained from nitration of 2-methylimidazole.

# 2-Methoxy-2-methyl-4,5-imidazolidinedione (10)

The substance was found to be readily formed in an attempted synthesis of 2-methyl-4,5-imidazoledione. Sodium (7.7 g, 0.34 mol) was dissolved in 300 ml of methanol and acetamidine hydrochloride(9.6 g, 0.10 mol) was added to the solution. The mixture was allowed to stand with mixing during 15 min and then a solution of diethyloxalat (15.1 g, 0.103 mol) in 100 ml of methanol was added dropwise during 3 h. The reaction mixture was treated with gaseous hydrogen chloride to obtain pH 5. The precipitate of NaCl formed was removed by filtration and the filtrate was concentrated at reduced pressure at 30-35 °C to 70-80 ml. The white precipitate formed was removed by filtration, dried at 40 °C and proved to be a mixture of organic product and sodium chloride. After extraction with acetone using a Soxhlet apparatus the organic product was shown by <sup>1</sup>H NMR to be a mixture of 2-methyl-4,5-imidazolidinedione (9) and 2-methoxy-2-methyl-4,5-imidazolidinedione (10). When recrystallised from methanol all 2-methyl-4,5imidazoledione was transformed to (10) and gave a total of 9.6 g (64 %) of 2-methoxy-2-methyl-4,5-imidazolidinedione; mp 158 °C (dec.). IR (KBr): 3249 (NH), 1755 (C=O) 1477, 1427, 1388, 1176, 1124, 1047, 790, 729, 674, 597 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 1.56 (s, 3H, CH<sub>3</sub>), 2.97(s, 3H, O-CH<sub>3</sub>), 9.98 (s, 2H, NH) ppm. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>) δ 27.2, 48.2, 92.0, 160.2. The mixture with 9 gave in addition the following <sup>1</sup>H NMR signals (DMSO-d<sub>6</sub>)  $\delta$  1.50 (s, 3H, CH<sub>3</sub>), 9.65 (s, 1H, NH) ppm; Anal. Calcd for C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>: C, 41.67; H, 5.65; N, 19.30. Found: C 41.49; H, 5.59; N, 19.44.

#### Independent synthesis of 4 from 2-methoxy-2-methyl-4,5-imidazolidinedione (10)

The dione (1.44 g, 10 mmol) was dissolved at 15-20 °C in sulfuric acid (d 1.84, 6.0 ml) and nitric acid (1.1 ml, 2.6 mmol) was added dropwise during 5 minutes, the temperature being kept below 30 °C by external cooling. After 10 minutes a precipitate of 2-(dinitromethylene)-4,5-imidazoledione was formed, which was removed by filtration, washed by trifluoroacetic acid (3 x 5 ml) and dried under vacuum at room temperature to give 1.36 g (67 %) of pure substance. Spectral analysis proved the product to be identical with compound **4**.

# 1,1-Diamino-2,2-dinitroethylene (5)

2-(Dinitromethylene)-4,5-imidazoledione (1.25 g, 6.20 mmol) was suspended in water (5 ml) and 25 % aqueous ammonia (2 ml) was added to obtain pH 8-9. The white solid dissolved immediately and in a few seconds bright yellow crystals precipitated (1,1-diamino-2,2-dinitroethylene). The precipitate was washed with water and dried at 50 °C to give 0.8 g (87 %) of 1,1-diamino-2,2-dinitroethylene. IR. (KBr): 3417 (NH<sub>2</sub>), 3315 (NH<sub>2</sub>), 3200 (NH<sub>2</sub>), 1638 (NH<sub>2</sub>), 1524 (NO<sub>2</sub>), 1471, 1400, 1356 (NO<sub>2</sub>), 1234, 1176, 1143, 1027, 752, 652, 521, 462 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$  8.77 ppm.<sup>13</sup>C NMR (DMSO-d<sub>6</sub>)  $\delta$  128.5, 158.8; MS *m/e* 148 (M<sup>+</sup>); Anal. Calcd for C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>O<sub>4</sub>: C, 16.22; H, 2.72; N, 37.84. Found: C, 16.06; H, 2.62; N, 37.68.

Treatment of the aqueous phase with calcium nitrate after removal of **5** lead to quantitative precipitation of calcium oxalate.

# 2-(Dinitromethylene)-tetrahydroimidazole (6)

Sodium hydride (96 mg, 4.0 mmol) was added in portions to a stirred solution of 1,1diamino-2,2-dinitroethylene (296 mg, 2.00 mmol) under nitrogen in dry N,Ndimethylformamide (6.0 ml) at 25°C. When the evolution of hydrogen had ceased (5-10 min), 1,2-dibromoethane (368 mg) was added. After 2 h at 115°C the reaction mixture was allowed to reach room temperature. Addition of water containing acetic acid (0.3ml) gave the crude product, which was recrystallised from toluene/diisopropylether, giving 250 mg (70 %) mp 261-262 °C (lit<sup>6</sup> 261-262 °C). The product was spectroscopically (IR and NMR) identical with previously prepared 2-(dinitromethylene)-tetrahydroimidazole<sup>6</sup>.

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