

# The Synthesis of Amino- and Nitro-Substituted Heterocycles as Insensitive Energetic Materials

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# The Synthesis of Amino- and Nitro-substituted Heterocycles as Insensitive Energetic Materials

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## Abstract

In this paper we will describe the synthesis of several amino- and nitro-substituted heterocycles, examples from a continuing research project targeted at the synthesis of new, insensitive energetic materials that possess at least 80% the power of HMX (28% more power than TATB). Recently we reported the synthesis and scale-up of the insensitive energetic material, 2,6-diamino-3,5-dinitropyrazine-1-oxide (**LLM-105**). The energy content (81% the power of HMX) and thermal stability of **LLM-105** make it a viable candidate material for insensitive boosters and deep oil perforation. We will report on recent synthetic improvements and several performance and safety tests performed on **LLM-105**, including a 1 in. cylinder shot and plate dent. We will also report on the synthesis and characterization of 4-amino-3,5-dinitropyrazole (**LLM-116**), an interesting new insensitive energetic material with a measured crystal density of 1.90 g/cc, to our knowledge the highest density yet measured for a five-membered heterocycle containing amino- and nitro-substituents. **LLM-116** was synthesized by reacting 3,5-dinitropyrazole with 1,1,1-trimethylhydrazinium iodide (**TMHI**) in DMSO in the presence of base. The synthesis and characterization of 4-amino-5-nitro-1,2,3-triazole (**ANTZ**) and 4,5-dinitro-1,2,3-triazole (**DNTZ**), first described by Baryshnikov and coworkers, will also be presented along with the synthesis of several new energetic materials derived from **ANTZ** and **DNTZ**.

The Synthesis Group of the Energetic Materials Program Element at LLNL is dedicated to developing new energetic compounds with enhanced performance and sensitivity characteristics as replacements for energetic materials currently in the stockpile. Recently our research efforts have concentrated on the synthesis of heterocyclic compounds substituted with both amino- and nitro- substituents. These new compounds have included 2,6-diamino-3,5-dinitropyrazine-1-oxide (**LLM-105**)<sup>1</sup>, 4-amino-3,5-dinitropyrazole (**LLM-116**)<sup>2</sup>, insensitive energetic materials with 81-90% the energy of HMX. The energy content of these compounds

make them very interesting for several applications, including insensitive boosters, detonators and possibly main charges in specialty munitions.

LLM-105 was synthesized by a modification of a procedure described in a Russian patent.<sup>3</sup> In the research and development stage of the scale-up process we made significant improvements to the yields and ease of work-up of the Russian procedure. The synthesis of LLM-105 currently involves reacting commercially available 2,6-dichloropyrazine with sodium methoxide to yield 2-methoxy-6-chloropyrazine, followed by nitration with mixed acid at 45 °C for 18h to yield 2-chloro-6-methoxy-3,5-dinitropyrazine (70% yield). This is treated with NH<sub>4</sub>OH in CH<sub>3</sub>CN at 60 °C to yield 2,6-diamino-3,5-dinitropyrazine (ANPZ).<sup>4</sup> Oxidation of ANPZ with a mixture of trifluoroacetic acid and 30% H<sub>2</sub>O<sub>2</sub> yielded LLM-105 (in 51% overall yield) from 2,6-dichloropyrazine. (Fig. 1) The synthesis of **LLM-105** is an illustration of the

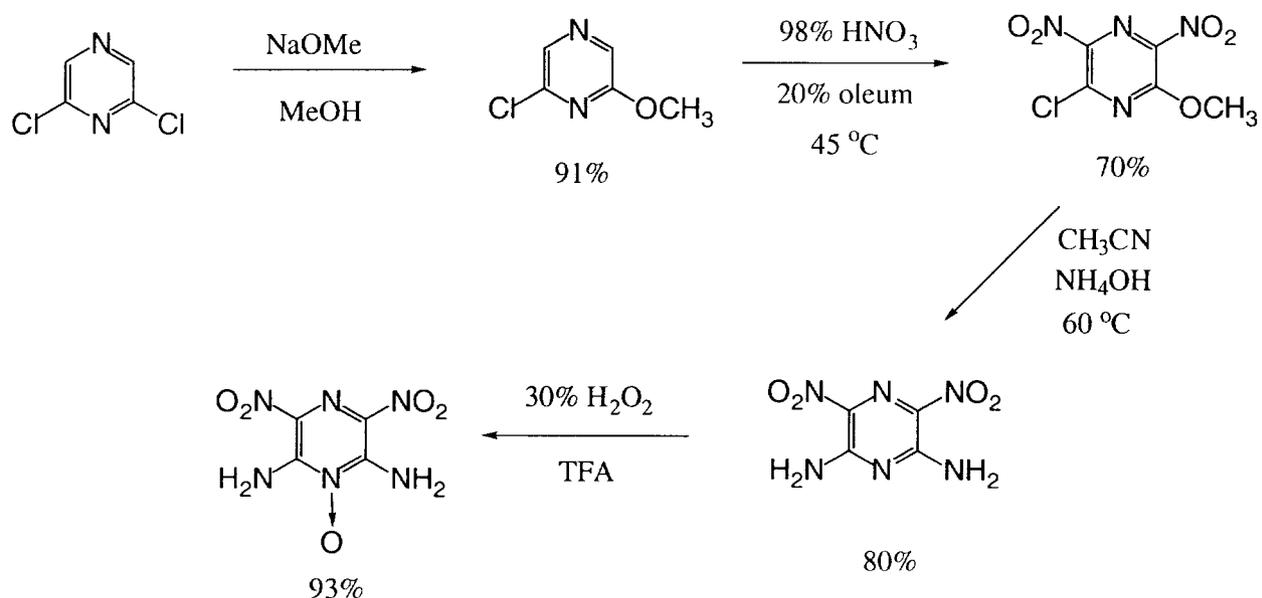


Fig. 1. Synthesis of LLM-105.

classical approach to the synthesis of nitro-substituted heterocycles. In general electron-deficient heterocycles such as pyrazines or pyridines do not undergo electrophilic substitution

reactions (nitration) under normal conditions unless substituted with electron-donating substituents. This is illustrated in our attempted nitration of 2,6-dichloropyrazine which gave a low yield of an unidentified mixture of products, but the addition of the electron-donating methoxy substituent allowed the nitration to run smoothly at 45 °C. Recently we found the treatment of 2,6-dimethoxypyrazine, an even more activated pyrazine ring system, at room temperature with 100% HNO<sub>3</sub>/100% H<sub>2</sub>SO<sub>4</sub> gave 2,6-dimethoxy-3,5-dinitropyrazine in 62% yield.(Fig. 2) This may be converted to ANPZ under the conditions used above in 98% yield. We also investigated the nitration of 2,6-dimethoxypyrazine with KNO<sub>3</sub>/100% H<sub>2</sub>SO<sub>4</sub> which gave 2,6-dimethoxy-3,5-dinitropyrazine in 72% yield but contained about 8% of an unidentified impurity. We plan on using the 2,6-dimethoxy-3,5-dinitropyrazine intermediate in further syntheses of LLM-105 because it can be synthesized at room temperature with little sacrifice in yield compared to the original synthesis.

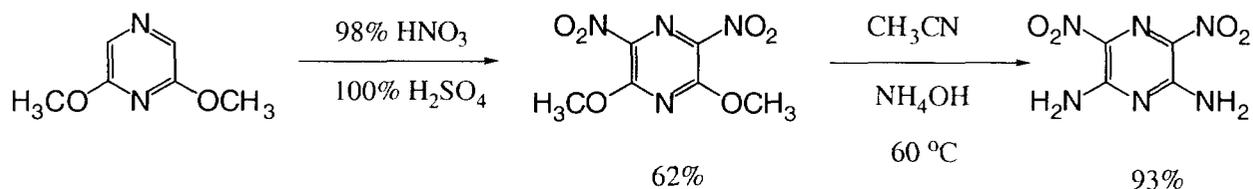


Fig. 2. Synthesis of 2,6-dimethoxy-3,5-dinitropyrazine

LLM-105 has some very attractive physical properties: a density of 1.918 g/cc<sup>5</sup>, a decomposition point of 354 °C, and a drop hammer (Dh<sub>50</sub>) value of 60-120 cm. A total of about 2Kg of LLM-105 has been synthesized in our laboratories which was enough material to perform a 1 in cylinder shot performance measurement, a series of Floret tests (which measures initiability, energy output and divergence of explosives), and one-dimensional shock sensitivity measurements. The 1 inch cylinder shot confirmed the predicted performance and the shock sensitivity measurements, although performed at low theoretical maximum density (88%

TMD), showed LLM-105 has similar sensitivity properties to 1,3,5-triamino-2,4,6-trinitrobenzene (**TATB**) pressed to similar TMD. The series of Floret tests showed RX-55-AE (97.5% LLM-105 / 2.5% Viton A binder) to significantly outperform Ultra-fine TATB (**UF-TATB**) in terms of higher energy output and better divergence characteristics. LLM-105 also showed superior performance to UF-TATB by requiring smaller flyer plates for initiation at both ambient and cold temperatures. We also investigated the performance of 2,6-diamino-3,5-dinitropyrazine (**ANPZ**)<sup>5</sup> in the Floret test. ANPZ has a crystal density of 1.84 g/cc<sup>5</sup> and is predicted to have similar energy output to TATB. ANPZ was ground to finer particle size to produce morphology similar to UF-TATB. The Floret test performed on the ground ANPZ showed a “go” at ambient temperature with higher energy and better divergence than UF-TATB.

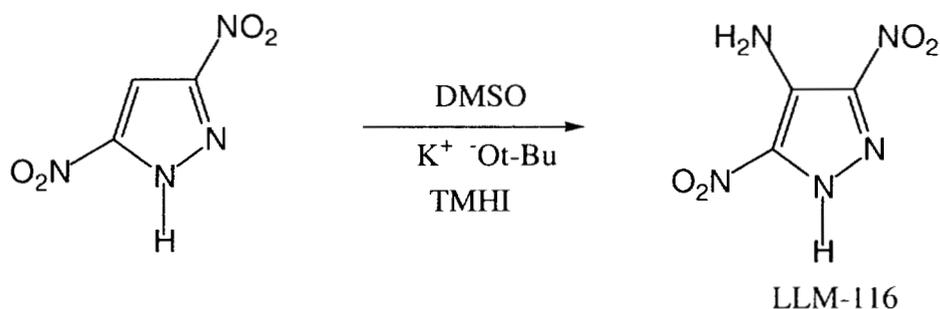


Fig. 3. Synthesis of LLM-116.

Recently we reported the synthesis of TATB by the nucleophilic amination of picramide with 1,1,1-trimethylhydrazinium iodide (**TMHI**)<sup>6</sup> or 4-amino-1,2,4-triazole (**ATA**)<sup>7</sup> by the Vicarious Nucleophilic Substitution of hydrogen (VNS).<sup>8,9,10</sup> This synthesis took advantage of the electrophilic nature of nitro-substituted aromatics and represented a non-classical approach to the synthesis of amino- and nitro-substituted aromatics. This new approach was subsequently used in the synthesis of 4-amino-3,5-dinitropyrazole (**LLM-116**). LLM-116 was synthesized in 70% yield from 3,5-dinitropyrazole by treatment with **TMHI** (in DMSO) in the presence of 2

equivalents of potassium *t*-butoxide.(Fig. 3) LLM-116 has a density of 1.90 g/cc<sup>5</sup>, a decomposition point of 178 °C and has a Dh<sub>50</sub>= 165cm. LLM-116 is predicted to have 90% the power of HMX.

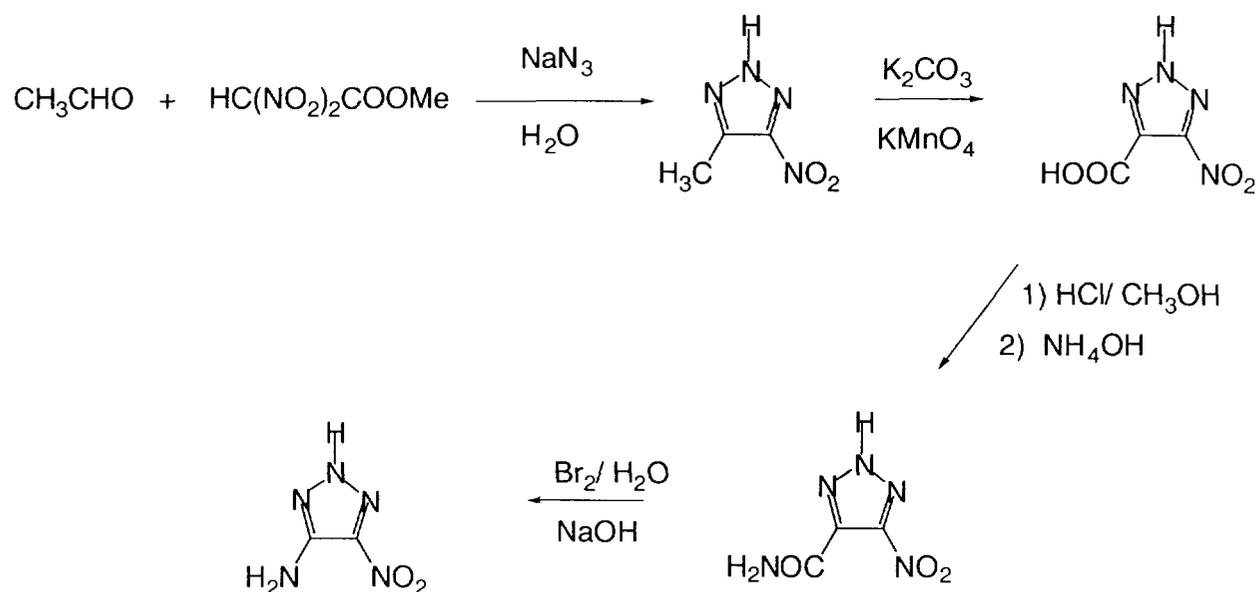


Fig. 4. Synthesis of ANTZ

Recently we synthesized 4-amino-5-nitro-1,2,3-triazole (ANTZ) following a procedure described by Shevelev and coworkers.<sup>11</sup>(Fig. 4) The synthesis involved the condensation of acetaldehyde with ethyl-2,2-dinitroacetate in the presence of NaN<sub>3</sub> to yield 3-methyl-5-nitro-1,2,3-triazole. This was oxidized to 3-carboxy-5-nitro-1,2,3-triazole which was converted by standard chemistry to ANTZ . ANTZ has a decomposition point of 297 °C, showing better thermal stability than 5-amino-3-nitro-1,2,4-triazole (ANTA).<sup>12,13,14</sup> ANTZ has a Dh<sub>50</sub>=154 cm and is not spark or friction sensitive. We are in the process of growing crystals of ANTZ for x-ray crystallographic analysis. In an analogous manner to the synthesis of ANTA derivatives,<sup>13,15</sup> ANTZ was reacted with a series of chloro-substituted nitroaromatics to yield ANTZ-substituted energetic materials. 4,6-bis(4-amino-5-nitro-1,2,3-triazol-2-yl)-5-nitropyrimidine (LLM-131),

2,4-bis(4-amino-5-nitro-1,2,3-triazol-2-yl)-5-nitropyrimidine (**LLM-132**), and 2-(4-amino-5-nitro-1,2,3-triazol-2-yl)-3,5-dinitropyridine (**LLM-133**) were synthesized by reacting ANTZ in refluxing CH<sub>3</sub>CN in the presence of base with 4,6-dichloro-5-nitropyrimidine, 2,4-dichloro-5-nitropyrimidine, and 2-chloro-3,5-dinitropyridine, respectively. We are in the process of characterizing these new compounds. ANTZ was also oxidized with 30% H<sub>2</sub>O<sub>2</sub> and conc. H<sub>2</sub>SO<sub>4</sub> to yield 4,5-dinitro-1,2,3-triazole (**DNTZ**)<sup>11</sup> which was isolated as the potassium salt by treatment with KOH in EtOH. We are currently investigating the synthesis of the ammonium salt of DNTZ for possible application as a propellant ingredient.

### References

1. P. F. Pagoria, A. R. Mitchell, R. D. Schmidt, R. L. Simpson, F. Garcia, J. Forbes, J. Cutting, R. Lee, R. Swansiger, and D. M. Hoffman, Presented at the Insensitive Munitions and Energetic Materials Technology Symposium, San Diego, CA, 1998.
2. P. F. Pagoria, A. R. Mitchell, and R. D. Schmidt, Presented at the 211th American Chemical Society National Meeting, New Orleans, LA, March 24-28, 1996.
3. Russian Patent SU 1703645A1. Cheeseman, Goodwin, *J. Chem. Soc.*, (1971), 2973.
4. D.S. Donald, U.S. Patent 3,808,209, Apr. 30, 1974.
5. R. Gilardi, X-ray crystallographic determination, Naval Research Laboratory, Washington, D.C.
6. P. F. Pagoria, A. R. Mitchell, and R. D. Schmidt, *J. Org. Chem.*, 61, (1996) 2934.
7. A. R. Katritzky and K. S. Lorenzo, *J. Org. Chem.*, 51, (1986) 5039.
8. A. R. Mitchell, P. F. Pagoria, and R. D. Schmidt, U.S. Pat. No. 5,569,783, Oct. 29, 1996.
9. A. R. Mitchell, P. F. Pagoria, and R. D. Schmidt, U.S. Pat. No. 6,069,277, May 30, 2000.
10. A. R. Mitchell, P. F. Pagoria, and R. D. Schmidt, U.S. Pat. No. 5,633,406, May 27, 1997.

11. A. T. Baryshnikov, V. I. Erashko, N. I. Zubanova, B. I. Ugrak, S. A. Shevelev, A. A. Fainzilberg, A. L. Laikhter, L. G. Melnikova, and V. V. Semenov, *Bull. Russ. Acad. Sci., Chem. Ser.*, 41, (1992) 751.
12. M. S. Pevzner, T. N. Kulibabina, N. A. Povarova, and L. V. Kilina, *Chem. Heterocycl. Comps.*, (1979) 929.
13. K. Y. Lee, C. B. Storm, M. A. Hiskey, and M. D. Coburn, *J. Energet. Mat.*, 9, (1991) 415.
14. R. L. Simpson, P. F. Pagoria, A. R. Mitchell, and C. L. Coon, *Propell. Explos. Pyrotech.*, 19, (1994) 174.
15. P.F. Pagoria, unpublished results.

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