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Nitroureas II. Synthesis of Bicyclic Mono- and Dinitrourea Compounds(*)

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Nitroharnstoffe II. Synthese von bizyklischen Mono- und Dinitroharnstoff-Verbindungen

Es wird über die Synthese und Charakterisierung verschiedener bizyklischer Mono- und Dinitroharnstoff-Verbindungen als energiereiche Komponenten berichtet und ihre Verwendung als Vorstufe für andere energiereiche Verbindungen diskutiert. Das neue Nitrolyse-Reagenz, Trifluormethansulfonsäureanhydrid/20% N_2O_5/Salpetersäure, wird ebenfalls beschrieben.

Nitro-urées II. Synthèse de composés bicycliques mono-urée et dinitro-urée

On décrit la synthèse et la caractérisation de différents composés bicycliques monourée et dinitro-urée en tant que composants énergétiques et leur utilisation comme précurseurs pour d'autres compositions énergétiques. On décrit également le nouveau réactif de nitrolyse, l'anhydride d'acide trifluorométhanesulfonique/20% N_2O_5/acide nitrique.

Summary

We report the synthesis and characterization of several bicyclic mono- and dinitrourea compounds as energetic materials and discuss their use as precursors to other energetic compounds. The new nitrolyzing reagent, trifluoromethanesulfonic acid anhydride/20% N_2O_5/nitric acid, will also be described.

1. Introduction

As part of a broad program to develop new, energetic materials which (1) are insensitive and perform better than 1,3,5-triamino-2,4,6-trinitrobenzene (**TATB**); and (2) have better performance[1] than 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (**HMX**); we have synthesized several, new, cyclic and bicyclic mono- and dinitrourea compounds. In a previous paper we reported the synthesis, scale-up, and characterization of an interesting new dinitrourea, 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (**K-6**)[2a], which has a density[2b] of 1.932 g/cm^3 and 3–5% more energy than HMX. In this paper we describe the synthesis and characterization of the mono- and dinitrourea compounds: 2,4,6-trinitro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3-one (*1*), 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3-one (*2*), 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (*3*), and 2,5,7-trinitro-2,5,7,9-tetraazabicyclo[4.3.0]-nonane-8-one (*4*), and the hydrolysis of compounds (*3*) and **K-6**.

The properties of nitrourea compounds suggest they would make excellent candidates as both insensitive and highly energetic materials, and also serve as precursors of other energetic compounds: (1) the urea moiety has an inherent high molecular density, suggesting that the mono- and dinitrourea derivatives should also have attractive molecular densities. This was supported by the work of Minsky[3] at Picatinny Arsenal who first nitrated glycoluril using 100% HNO_3 and P_2O_5 at 50 °C to yield tetranitroglycoluril (**TNGU**), which has one of the highest densities of known organic materials (2.04 g/cm^3). 1,4-Dinitroglycoluril (**DNGU**), the mono-nitrourea analog of TNGU, also has an attractive crystal density[4] of 1.992 g/cm^3; (2) The dinitrourea moiety is oxygen-rich which adds greatly to the oxygen balance of a compound; (3) The mononitrourea compounds, with their intermolecular hydrogen bonding, may be candidates as insensitive energetic materials; and (4) The dinitrourea moiety is easily hydrolyzed[5] to yield open-chain, bis-nitroamino compounds.

2. Synthesis of 2,4,6-Trinitro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3-one (*1*) and 2,4,6,8-Tetranitro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3-one (*2*)

The preparation and subsequent nitration of 2,4,6,8-tetraazabicyclo[3.3.0]octan-3-one dihydrochloride salt (*5*) to yield 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3.3.0]octan-3-one (*2*) was first described by Wenjie and coworkers[6]. Compound (*2*) was considered interesting as an intermediate in a more efficient route to 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3.3.0]octane (*6*), first synthesized in our laboratories[7]. In an attempt to reproduce the synthesis of compound (*2*), we found that if the reaction temperature was maintained at <15 °C the nitration does not go to completion and compound (*1*) precipitates from the reaction mixture in 53% yield. When the reaction temperature is raised to 20–50 °C, the nitration is complete, and compound (*2*) is obtained exclusively in 40% yield (Fig. 1). These results initiated a study of the effects of temperature and nitration reagent on the yields of (*1*) and (*2*) (Table 1). It was found that the use of 90% HNO_3/Ac_2O as the nitrating agent at 0–40 °C gave exclusively (*1*) in 72% yield while the use of 100% HNO_3/trifluoroacetic anhydride (**TFAA**), a powerful nitrating agent, gave exclusively (*2*) over the same temperature range. Compound (*1*) proved to be

(*) Nitroureas I, see *Propellants, Explos., Pyrotech. 19*, 202 (1994)

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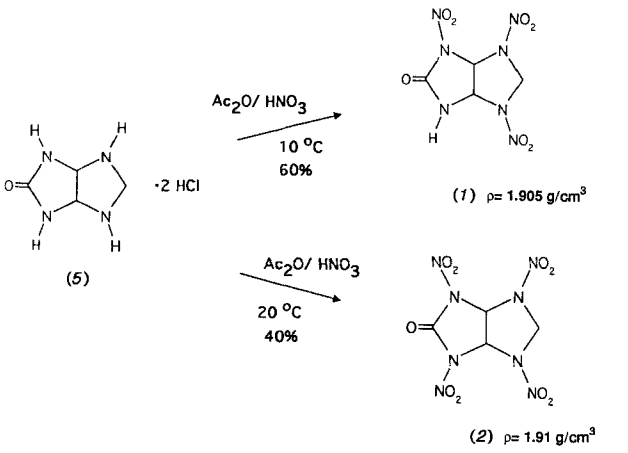

Figure 1. Synthesis of compounds (*1*) and (*2*) from (*5*).

interesting because of its high density[8] ($\varrho = 1.905$ g/cm^3) and relative insensitivity to shock (61 cm on the drop hammer machine versus 32 cm for HMX). TIGER code calculations suggest it has approximately the same energy as HMX[1].

Because of the interesting properties of compounds (*1*) and (*2*) the synthesis of the homologous bicyclo[4.3.0]nonane series was undertaken. We report[9] the synthesis of 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo-[4.3.0]nonane-8-one (*3*) and 2,5,7-trinitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (*4*). Compound (*3*) was especially interesting[9] with a crystal density of 1.969 g/cm^3. The synthesis of (*3*) involved the first use of the new nitrolysis reagent, trifluoromethanesulfonic acid anhydride (**TFMSAA**)/20% N_2O_5/HNO_3.

Table 1. Effect of Nitrating Agent on Product Yields of (*1*) and (*2*)

	90% HNO_3/Ac_2O	100% HNO_3/Ac_2O	100% HNO_3/TFAA
Compound (*1*)	72%	53% (<15 °C)	0
Compound (*2*)	0	49% (20–50 °C)	51%

3. Synthesis[10] of 2,5,7,9-Tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (*3*) – Use of a new, powerful nitrolysis reagent, trifluoromethanesulfonic acid anhydride/20% N_2O_5/HNO_3

The synthesis of (*3*) and (*4*) involved a multi-step reaction sequence in which 1,3-diacetyl-2-imidazolone (*7*) is brominated[11] and reacted with ethylenedinitramine (**EDNA**)[12] in the presence of triethylamine to yield a mixture of 7.9-diacetyl-2,5-dinitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (*8*) and 7-acetyl-2,5-dinitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (*9*) (Figure 2)[13]. The diacetyl compound is easily converted to the mono-acetyl derivative by treatment with ammonium hydroxide in CH_3CN with an overall yield of (*9*) of 32%. Nitration of (*9*) with a 20% N_2O_5/HNO_3 mixture[14] at room temperature yielded 7-acetyl-2,5,9-trinitro-2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one (*10*) in 80% yield. The nitrolysis of the final acetyl group proved to be

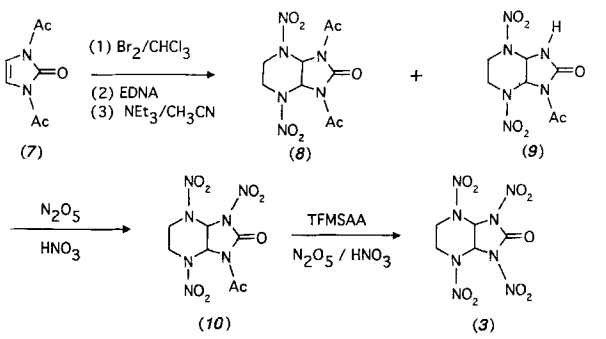

Figure 2. Synthesis of 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (*3*).

very difficult. Several nitrolysis reagents were tried (20% N_2O_5/HNO_3 at 25–50 °C, TFAA/20% N_2O_5/HNO_3 at 20–40 °C, Ac_2O/20% N_2O_5/HNO_3 at 25–50 °C and TFAA/100% HNO_3) but all resulted in recovery of starting material. The development of the new, powerful nitrolysis reagent, trifluoromethanesulfonic acid anhydride (TFMSAA/20% N_2O_5/HNO_3, allowed the nitrolysis of the final acetyl group to give (*3*) in 69% yield.

4. Synthesis of 2,5,7-Trinitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (*4*)

Because of the interest in the mononitrourea, (*1*), as an insensitive energetic material, the synthesis of the homologous compound (*4*), was investigated. The hydrolysis of (*10*) with aqueous HCl in refluxing CH_3CN gave (*4*) in 85% yield (Fig. 3). The low crystal density[15] of 1.84 g/cm^3 precludes this compound from being of interest as a useful energetic material. Nitration of (*4*) with 20% N_2O_5/HNO_3 at 40 °C gave (*3*) in 90% yield, providing an alternative method for the synthesis of (*3*).

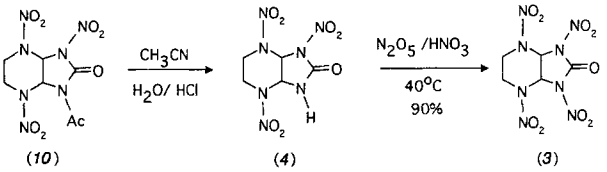

Figure 3. Synthesis of (*3*) and (*4*).

5. Hydrolysis of Dinitroureas

The interest in dinitroureas arose from their considerations as precursors to important intermediates in the synthesis of other energetic materials. The interest in **K-6** arose from its consideration as a precursor to 1,3,5-trinitro-1,3,5-triazapentane (**TTP**) (*12*) (Fig. 4), an intermediate to the synthesis of polyazabicyclo[5.3.0]decane compounds (Fig. 5). The carbonyl function of cyclic dinitrourea compounds have been reported to be easily hydrolyzed to yield open-chain dinitramino compounds[5d-h]; e.g., the known energetic material, ethylenedinitramine (**EDNA**) (*13*) may be synthesized by the hydrolysis of 1,3-dinitroimidazolidi-

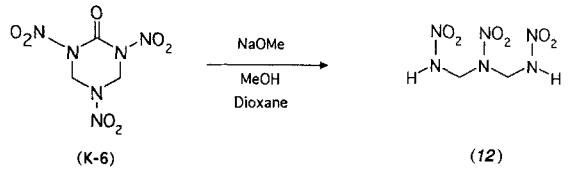

Figure 4. Hydrolysis of **K-6** to yield **TTP**.

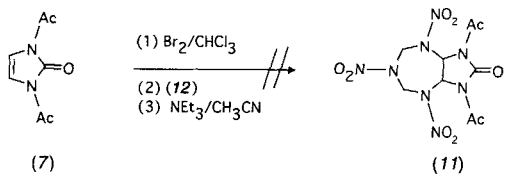

Figure 5. Condensation of **TTP** and 4,5-dibromo-1,3-diacetylimidazolidinone.

none[5h]. We found the heterogeneous methanolysis of **K-6** using sodium methoxide in a MeOH/dioxane mixture gave the disodium salt of (*12*), which upon acidification with ethereal HCl, gave (*12*) in 70% yield. L. T. Eremenko and coworkers[16a] were the first to describe the synthesis of (*12*) by heating methylenedinitramine (**MEDINA**) (*14*) in DMSO which disproportionates to a mixture of (*12*), (*14*) and 1,3,5,7-tetranitro-1,3,5,7-tetraazaheptane. We found that (*12*) also undergoes disproportionation in warm DMSO to a mixture of (*14*) and (*12*). This disproportionation seems to be rather facile since small amounts (*14*) were observed in the ^{1}H-NMR spectrum[16b] of the (*12*) obtained by methanolysis of **K-6**. Attempts at the condensation of (*12*) with 4,5-dibromo-1,3-diacetylimidazolidinone (made in situ by the reaction of bromine and 1,3-diacetylimidazolone[11] gave a complex mixture from which none of the desired 8,10-diacetyl-2,4,6-trinitro-2,4,6,8,10-pentaazabicyclo[5.3.0]decane-9-one (*11*) could be isolated. The major product was recovered 1,3-diacetylimidazolone (Fig. 5.).

Compound (*3*) was considered a precursor to 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane (*15*) through the hydrolysis of the dinitrourea function and subsequent ring-closure by condensation with formaldehyde. It was found that methanolysis of (*3*) with sodium methoxide followed by acidification with ethereal HCl gave 2,3-dinitramino-1,4-piperazine (*16*) in which the nitramino groups were in the *trans*-configuration instead of the expected *cis-configuration*[17] (Fig. 6). This suggests that under the reaction conditions the piperazine ring underwent ring opening, followed by epimerization, and subsequent ring closure to the more stable *trans*-configuration. This precludes any attempt to close the ring to give (*15*).

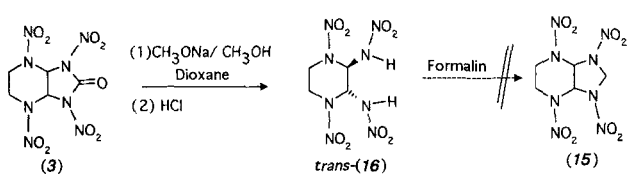

Figure 6. Hydrolysis of compound (*3*).

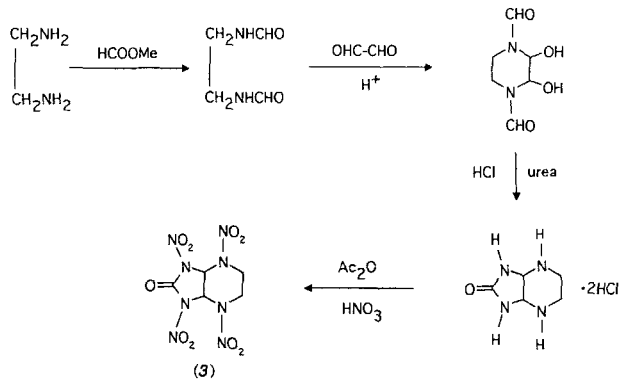

Figure 7. Alternative synthesis of (*3*) (Ref. 10).

Attempts have been made at the methanolysis in the presence of formalin in the hope of that the *cis*-conformation could be trapped, but thus far this has been unsuccessful. At room temperature this yields a product whose ^{1}H-NMR spectrum suggests it is the ring-opened carbamate. Upon heating, the bicyclic system is destroyed and only **EDNA** (*13*) is isolated.

6. Experimental

2.4.6-Trinitro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3-one (1)

A sample of 39 ml (41.3 mmol) of acetic anhydride was added with stirring at <15 °C to 19.5 ml (43.3 mmol) of 90% HNO_3 over a 20 min period. The solution was cooled to 4 °C and 6.00 g (2.98 mmol) of (*5*) was added[6] portion-wise over a 20 min period, keeping the reaction temp <7 °C. The reaction mixture was allowed to warm to room temperature and stir overnight. The suspension was cooled to 4 °C and poured carefully into 200 g of ice water. The precipitate was collected by suction filtration, washed with 300 ml of water, and dried under vacuum at room temperature to yield 5.64 g (72%) of a white powder. Recrystallization from CH_3CN yielded 3.84 g (49% overall yield of white microcrystals); m.p. 196–197 °C. IR (KBr) 3225, 3170 (N–H), 3015, 2950, 2916, 2850 (C–H), 1801 (C=O), 1597, 1580, 1536, 1400, 1378, 1365 (NO_2), 1480, 1460, 1438 (C–H), 1300 [cm^{-1}]; ^{1}H-NMR (CD_3CN): δ 5.33, 5.54, 6.32, 6.54 (AA′BB′ quartet, 2H, CH_2–), 6.12, 6.14, 6.24, 6.26, 7.41, 7.53 (AA′BB′ quartet with N–H splitting, 2H, Bridgehead C–H), 7.63 (broad s, 1H, N–H); Anal.: Calcd for $C_4H_5N_7O_7$: C, 18.26; H, 1.92; N, 37.26. Found: C, 19.10; H, 1.97; N, 37.25. Structure was confirmed[8] by X-ray crystallographic analysis; ϱ = 1.905 g/cm^3.

2,4,6,8-Tetranitro-2,4,6,8-tetra-azabicyclo[3.3.0] octane-3-one (2)

Compound (*2*) was synthesized by the method of Wenjie and coworkers[6]. X-ray crystallographic analysis performed on this material gave[8] a crystal density of 1.91 g/cm^3.

2,5,7,9-Tetranitro-2,5,7,9-tetra-azabicyclo[4.3.0] nonane-8-one (3)

Method A: A 1 g sample of 20% N_2O_5/HNO_3 was added dropwise with stirring to a cold sample (−10 °C) of 1 ml (1.67 g) (5.3 mmol) of trifluoromethanesulfonic acid anhydride (TFMSAA) under an argon blanket. The mixture was stirred 5 min at −10 °C and then 0.2 g (0.63 mmol) of (*10*) was added. The cooling bath was removed and the mixture was heated to 70 °C for 2 h under argon. A voluminous white mass formed which was broken up and collected by suction filtration. The fuming solid was washed with 15 ml of CH_2Cl_2 to remove excess TFMSAA and then dissolved in 20 ml of CH_3CN. This solution was treated with 5 g of silica gel to remove impurities, the silica gel was removed by filtration, and the resulting solution was evaporated. The resulting sticky powder was collected by suction filtration and dried under vacuum at room temperature overnight to yield 0.19 g (94%) of a white powder. Recrystallization from EtOAc/toluene yielded 0.14 g (69%) of white microcrystals; m.p. 203–204 °C; IR (KBr) 3005, 2996, 1811, 1610, 1605, 1540, 1447, 1360 [cm^{-1}]; ^{1}H-NMR (CD_3CN) δ 3.7–4.9 (m, 4H, $-CH_2-$), 7.76 (s, 2H, C–H). Anal: Calcd for $C_5H_6N_8O_9$: C, 18.63; H, 1.86; N, 34.78. Found: C, 19.06; H, 1.91; N, 33.52. X-ray crystallographic analysis[8] gave a density of 1.969 g/cm^3.

Method B: To a solution of 150 ml of 20% N_2O_5/HNO_3 at −30 °C was added 0.5 g (1.8 mmol) of (*4*). The mixture was allowed to warm to room temperature and stirred 2.5 h and then heated at 45 °C for 2 h. The reaction mixture was cooled to room temperature are allowed to stir overnight. The solvent was removed under vacuum at room temperature to yield a white solid. Addition of 10 ml of water, collection by suction filtration, and drying under vacuum at room temperature yielded 0.52 g (90%) of a white powder whose ^{1}H-NMR was identical with an authentic sample.

2,5,7-Trinitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (4)

A solution of 4.79 g (15 mmol) of 10, 15 ml of 3 N HCl, and 80 ml of CH_3CN was refluxed for 2 h. The solution was allowed to cool to room temperature and stirred overnight. The solvent was reduced to 10 ml, the resulting precipitate was collected by suction filtration, and washed with 10 ml of water to yield 4.15 g (100%) of a white powder. Recrystallization from CH_3CN yielded 3.53 g (85%) of white microcrystals; m.p. 187–198 °C; ^{1}H-NMR (CD_3CN): δ 3.56–4.80 (m, 4H, $-CH_2-$), 6.26, 6.41, 7.45, 7.46, 7.61, 7.62 (AA′BB′ quartet, 2H, C–H), 8.00 (broad s, 1H, N–H). IR (KBr) 3352, 1802, 1572, 1562, 1322, 1306, 1298, 1274, 1232, 1185, 1080, 714 [cm^{-1}]. An X-ray crystallographic analysis[8] gave a density of 1.84 g/cm^3.

7,9-Diacetyl-2,5-dinitro-2,5,7,9-tetra-azabicyclo[4.3.0] nonane-8-one (8)

To a solution of 2.3 g (13.7 mmol) of 1,3-diacetyl-2-imidazolone (*7*)[11] in 7 ml of $CHCl_3$ cooled to 0 °C was added dropwise with stirring a solution of 2.25 g (14 mmol) of Br_2 in 5 ml of $CHCl_3$. The reaction mixture was allowed to warm to room temperature and stir 30 min. The solvent was removed and the resulting orange oil was dissolved in 15 ml of dry CH_3CN. To this was added a 2.42 g (16 mmol) sample of **EDNA**[12]. The resulting slurry was cooled to −7 °C, a solution of 2.94 g (29 mmol) of triethylamine in 4 ml of dry CH_3CN was added slowly dropwise, and the reaction mixture was allowed to stir at room temperature overnight. The reaction mixture was filtered to remove the triethylamine hydrochloride, the filtrate was taken, and the solvent was removed to yield an orange oily solid. Trituration with 10 ml of MeOH overnight yielded 1.3 g (35%) of a white powder which is a mixture of (*8*) and (*9*), predominantly (*9*). Compound (*8*) was obtained by "chromatotron" chromatography[18] of the above sample using 4% MeOH/$CHCl_3$ as the eluant ($R_f = 0.33$). Trituration of the sample obtained from the chromatography with 3 ml of MeOH yielded pure (*8*) as white microcrystals; m.p. 227–230 °C; IR (KBr). ^{1}H-NMR (CD_3CN): δ 2.53 (s, 6H, $-CH_3$), 3.10–4.78 (m, 4H, CH_2-), 7.20 (s, 2H, C–H). Anal: Calcd for $C_9H_{12}N_6O_7$: C, 34.18; H, 3.80; N, 26.58. Found: C, 34.15; H, 4.19; N, 26.09.

7-Acetyl-2,5-dinitro-2,5,7,9-tetra-azabicyclo[4.3.0] nonane-8-one (9)

To a 3.2 g (10 mmol) sample of (*8*) and (*9*) in 20 ml of CH_3CN of the mixture was added 1.1 g (18 mmol) of 28% NH_4OH and the mixture was heated to reflux 5 min and then allowed to stir at ambient temperature overnight. The resulting precipitate was collected by suction filtration to yield white microcrystals. The solvent was reduced in the filtrate to 2 ml to yield a second crop of white needles; Total yield: 2.9 g (91%). Recrystallization from CH_3CN yielded small microcrystals; m.p. 187–189 °C; IR (KBr) 3350, 3024, 1767, 1696, 1458, 1374, 1366, 1227, 1168 [cm^{-1}]. ^{1}H-NMR (CD_3CN) δ 2.50 (s, 3H, $-CH_3$), 3.04–4.90 (m, 4H, $-CH_2-$), 6.53, 6.69, 7.31, 7.32, 7.45, 7.46 (AA′BB′ quartet, 2H, C–H), 7.23 (broad s, 1H, N–H). Anal.: Calcd for $C_7H_{10}N_6O_6$: C, 30.66; H, 3.65; N, 30.66. Found: C, 30.70; H, 3.86; N, 30.66.

7-Acetyl-2,5,9-trinitro-2,5,7,9-tetra-azabicyclo[4.3.0] nonane-8-one (10)

To a solution of 19.7 g (36.5 mmol of N_2O_5) of 20% N_2O_5/HNO_3[14] at −30 °C was added portion-wise 2 g (7.3 mmol) of (*9*). The mixture was allowed to warm slowly to room temperature and then heated at 47 °C for 2 h. The reaction mixture was cooled and the solvent was removed under vacuum at room temperature to yield a gummy white solid. Trituration with 5 ml of dry CH_2Cl_2 allowed collection of a white powder by suction filtration; 2.3 g (100%). Recrystallization from CH_3CN yielded 1.86 g (80%) of white clumpy needles; m.p. 235–237 °C (from 208–220 °C material jumps around in melting point capillary tube); IR (KBr) 3100, 2998, 2948, 2849, 1804,

1722, 1600, 1540, 1454, 1180–1400 [cm^{-1}]. ^{1}H-NMR (CD_3CN): δ 2.43 (s, 3H, $-CH_3$), 3.33–4.80 (m, 4H, $-CH_2-$), 7.11, 7.13, 7.24, 7.26, 7.43, 7.56 (AA'BB' quartet, 2H, C–H). Anal: Calcd for $C_7H_9N_7O_8$; C, 26.33; H, 2.82; N, 30.72. Found: C, 26.33; H, 3.01; N, 29.76. An X-ray crystallographic analysis confirmed the structure[8].

Synthesis[15a] of 1,3,5-trinitro-1,3,5-triazapentane (12) from K-6

To a stirred suspension of 0.24 g (1 mmol) of **K-6** in 5 ml of dioxane was added dropwise 2.2 ml (2.2 mmol) of a 1 N NaOMe/MeOH. After addition the resulting gelatinous precipitate was collected by suction filtration and washed with 5 ml of acetone and 5 ml of ether. The slightly moist solid was added portion-wise with stirring to a saturated solution of ethereal HCl (50 ml). The mixture was stirred 45 min, filtered to remove any insoluble inorganic salts, and the solvent was removed to yield 2.0 g (100%) of a sticky white powder. Drying in a vacuum desiccator overnight yielded 1.3 g (65%) of a white solid. ^{1}H-NMR (DMSO-d_6): δ 5.48 (s, 2H, $-CH_2-$)[16 b].

Synthesis of trans-2,3-dinitramino-1,4-dinitropiperazine (16)

To a slurry of 0.32 g (1 mmol) of compound (*3*) in 8 ml of dioxane was added dropwise with stirring 2.2 ml of a 1 N NaOMe/MeOH solution and the heterogeneous mixture was allowed to stir 45 min. The gelatinous precipitate was collected by suction filtration and dried 3 h in a vacuum oven to yield 0.33 g (97%) of a white powder. This was dissolved in 3 ml of water and acidified with conc HCl to pH = 1. The solution was placed in the refrigerator overnight to yield a white precipitate which was collected by suction filtration and air-dried; 0.16 g (54%). Recrystallization from CH_3CN yielded 0.14 g of colorless plates: m.p. 126 °C (dec); ^{1}H-NMR (CD_3CN): δ 7.20 (s, 1H, C–H), 3.88–4.84 (m, 4H, $-CH_2-$), 3.80 (broad s, 2H, N–H). The structure was confirmed by X-ray crystallographic analysis[8]. The nitramino substituents were found to be in the *trans*-configuration.

7. References

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