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Synthesis of functional 2-substituted 1,3-dinitroimidazolidines. A new synthetic approach to high-energy compounds

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Abstract

Three new functional 2-substituted 1,3-dinitroImidazolidines were synthesized herein. A synthetic strategy is suggested for structurally different α,α-dinitraminocarboxylic acids via condensation of glyoxylic acid ethyl ester with amine or amide derivatives. Alkali- and acid-catalyzed hydrolyses of ethyl 1,3-dinitro-1,3-diazacyclopentane-2-carboxylate were studied. A series of hydrolysis products were isolated. The Curtius rearrangement of 1,3-dinitroimidazolidine-2-carboxylic acid to 2-isocyanato-1,3-dinitroimidazolidine was carried out. Hydrolyses of 1,3-dinitroimidazolidine-2-carbonyl azide and 2-isocyanato-1,3-dinitroimidazolidine were studied. 1,3-Dinitroimidazolidine-2-amine was captured as 1,3-bis(1,3-dinitroimidazolidin-2-yl)urea.

Keywords: 2-substituted 1,3-dinitroImidazolidines, nitrogen heterocycles, isocyanate, hydrolysis, Curtius rearrangement

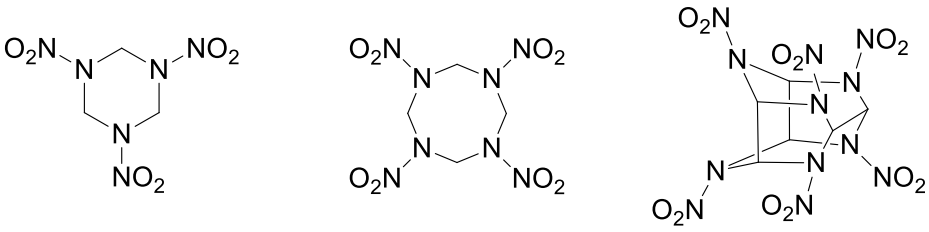
Introduction

Cyclic nitramines are high-energy-density compounds widely used in various composite explosives, rocket propellants, gun propellants and specialty chemicals. RDX and HMX that have been put to good use in defense and civil industries are the best known representatives in this class of compounds (Scheme 1). The design of new high-energy materials superior in detonation performance to the existing ones, as well as the development of their synthetic methods, is still a topical research area worldwide.[1]

Among the effective ways to improve energetic characteristics of explosive compounds is incorporating strained moieties such as five-membered rings or complex 2D or 3D molecules (cages) thereto. Predictions demonstrate that caged nitramines are much more attractive in seeking high-energy materials because they exhibit enhanced energetic characteristics and reduced sensitivity.[2] The density of nitramines increases with increasing molecular rigidity.[3] Such an approach can be exemplified by caged polynitro-substituted aza- and oxaazaisowurtzitanes, which are promising high-energy materials. These materials structurally contain strained moieties and have compact rigid molecules, which enhances their density and energetic performance.[4-11] 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.$0^{3,11}$.$0^{5,9}$]dodecane (CL-20, hexanitrohexaazaisowurtzitane, HNIW) (Scheme 1) is among the most powerful explosives domesticated by humankind (ρ = 0.044 g/cm^3, V_0D = 9.36 (ε) km/s).[12-14] It is viewed as a promising

component of composite explosives and as a eco-friendly high-energy oxidizer in rocket propellants, exhibiting a high specific impulse and oxygen balance.[15]

It is surprising that the hexaazaisowurtzitane system cannot be achieved through the ‘construction’ approach by stepwise addition of cycles. For instance, CL-20 is synthesized in two steps. At first, the isowurtzitane cage is built by condensation between glyoxal and primary amine or amide.[1] The next step is to convert the organic group of amine derivatives into the nitro group to obtain the energetic compound. Despite the promising outlook of CL-20, its application is limited due to the high synthesis cost.[1]



Scheme 1. Structural formulas of RDX, HMX and CL-20.

A significant problem arising during the synthesis of the hexaazaisowurtzitane cage is the selection of ammonia derivatives capable of generating this structure when condensed with glyoxal. In most cases, the isowurtzitane cage originates from condensation of primary amines that comprise an aromatic moiety or multiple bond linked to the amine group via a methylene bridge.[1] It has more recently been found that compounds similar to oxaazaisowurtzitane derivatives can be synthesized by condensation between sulfonamides and glyoxal.[16,17]

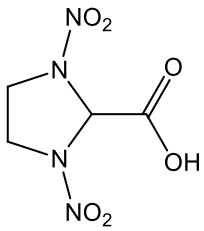
The development of synthetic methods for high-energy compounds bearing strained moieties and capable of being further transformed into more complex high-energy structures is a relevant science-based problem. Here we report the synthesis of three

novel energy-rich compounds bearing functional groups: α,α-dinitraminocarboxylic acid (carboxymethyl-nitramines), N,N'-(isocyanatomethylene)dinitramide (isocyanato-methylnitramines) and 1,3-bis[bis(nitroamino)methyl]urea (*sym*-dinitraminomethylureas).

The predictions demonstrate that the insertion of an amino group into linear nitramines improves their thermal stability.[18] In the case of 1,3,5-trinitrobenzene, the incorporation of three amino groups into its molecule (2,4,6-triamino-1,3,5-trinitrobenzene (TATB)) decreases solubility of the compound and enhances its density and thermal stability.[19-24]

Results and Discussion

In the course of this study, 1,3-dinitroimidazolidine-2-carboxylic acid (**1**) has been synthesized for the first time (Scheme 2).



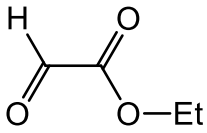
1

Scheme 2. 1,3-Dinitroimidazolidine-2-carboxylic acid.

The literature has no mention of the synthesis of imidazolidine-2-carboxylic acid or its derivatives by direct condensation. However, there are few data on the synthesis of analogous structures.[25-28]

Acid **1** was synthesized by three methods. In the first method (Method A), glyoxylic acid ethyl ester (**2**) was condensed with potassium ethylene-1,2-disulfamate (**3**) at pH=3.4 and 45–50°C to furnish potassium 2-(ethoxycarbonyl)imidazolidine-1,3-

disulfonate (**4**), which was then nitrated with concentrated HNO_3 at between -35°C and -30°C to ethyl 1,3-dinitroimidazolidine-2-carboxylate (**5**) (Schemes 3 and 4). The latter was subjected to acid-catalyzed hydrolysis in concentrated HCl upon boiling to target acid **1** (Scheme 4). The total yield of acid **1** by this method was 11.1% and the product had a high purity. Ester **2** was prepared by reacting diethyl L-tartrate with periodic acid in anhydrous diethyl ether.[29] A similar condensation method was used by Tartakovsky.[30]



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Scheme 3. Ethyl glyoxylate.

In the second method (Method B), compound **2** was condensed with ethylene dinitramine (**6**) in concentrated H_2SO_4 at lowered temperature (0–5°C) to yield ester **5** which was next acid-hydrolyzed in concentrated HCl upon boiling to acid **1** (Scheme 4). The total yield of acid **1** by this method was 9.8%. The first stage was based on Goodman's work in which paraformaldehyde was condensed with a range of linear nitramines (and with **6**) in concentrated H_2SO_4.[31] To avoid side reactions, Goodman's method was modified by reducing the reaction mixture temperature.

The third method (Method C) involved condensation between ester **2** and ethylenediamine (**7**) in acetic acid at 0–10°C followed by nitrosation of the resultant condensation product with nitrous acid at -5–0°C to ethyl 1,3-dinitrosoimidazolidine-2-carboxylate (**8**); nitration of the dinitroso derivative to compound **5**; and acid-catalyzed hydrolysis of **5** with boiling concentrated HCl to compound **1** (Scheme 4). The isolation of the condensation product was not performed. Nitrous acid was

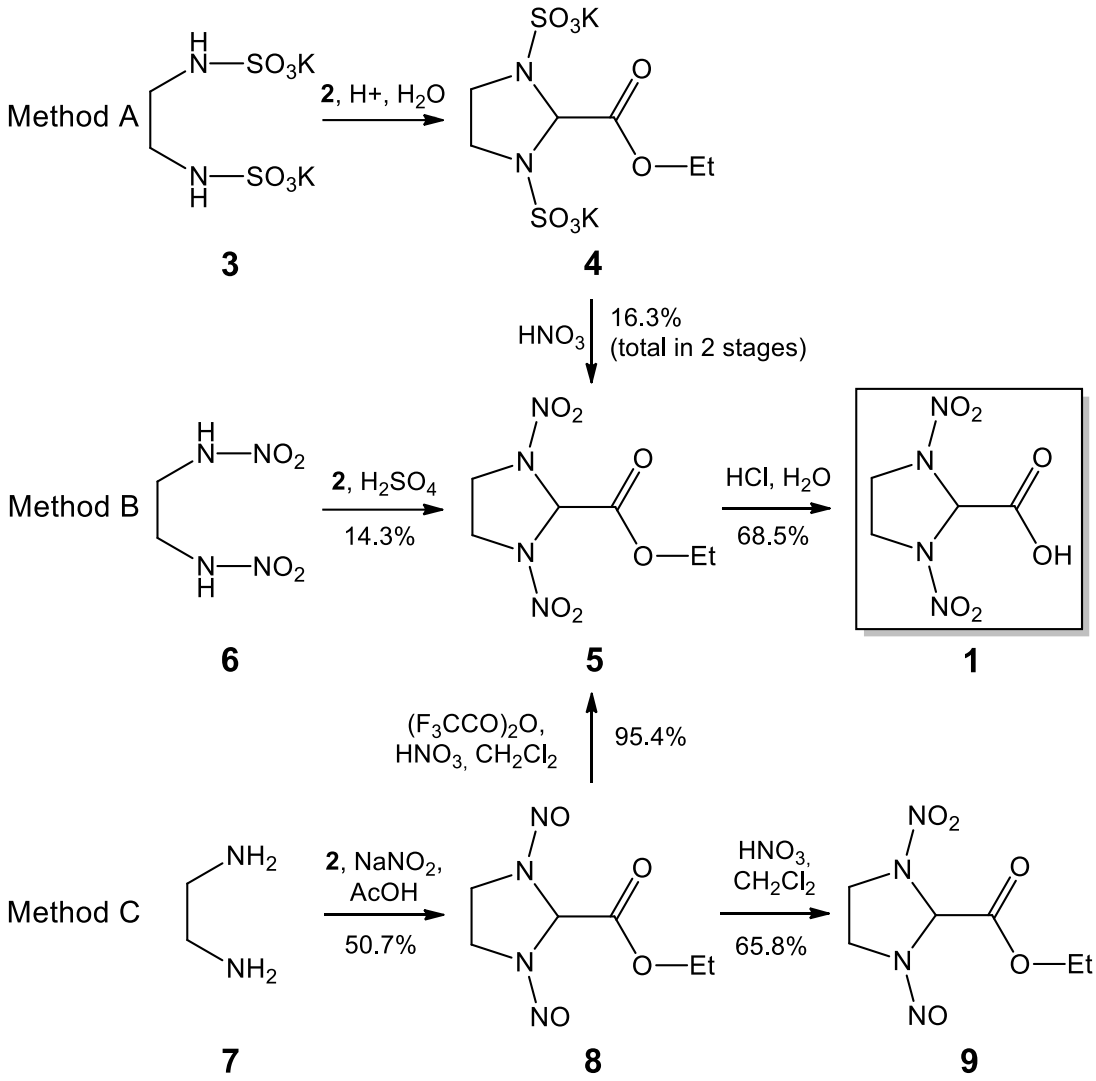
generated *in situ* from the reaction between sodium nitrite and acetic acid. Dinitroso derivative **8** could be nitrated either with mixed concentrated HNO_3/trifluoroacetic anhydride at between -15 and -10°C (95.4% yield) or with mixed concentrated HNO_3/nitric anhydride at between -35 and -30°C (67.8% yield). The maximum total yield of acid **1** by the third method was 33.1%. The condensation of ester **2** with compound **7** has not been described previously.

Nitration of compound **8** with concentrated HNO_3 or concentrated mixed nitric–sulfuric acids at reduced temperature did not result in ester **5**; instead, 1-nitroso-3-nitroimidazolidine-2-carboxylate (**9**) was formed in up to 65.8% yield.

The three developed methods for the synthesis of acid **1** are illustrated in Scheme 4.

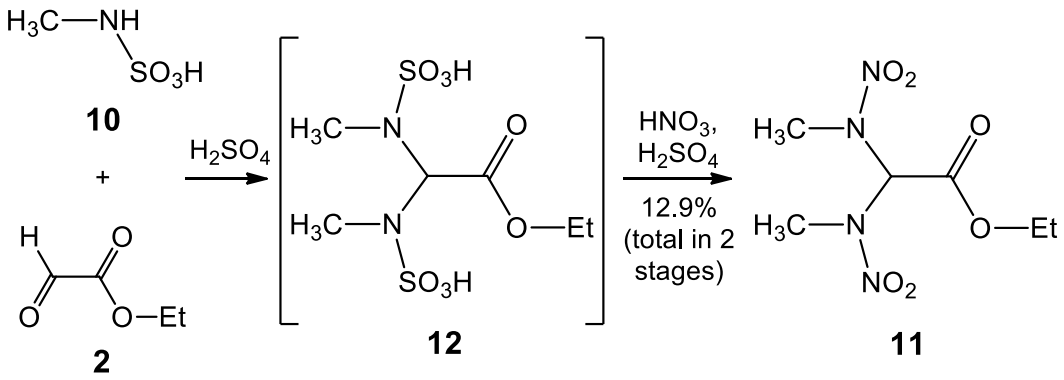
In all the three methods, the replacement of ethyl glyoxylate by glyoxylic acid or its salts (Na or K) diminished the yield considerably.

The use of carboxylic acid derivatives as starting reagents for the synthesis of cyclic nitramines constitutes a novel synthetic strategy for these compounds.



Scheme 4. Synthetic methods for 1,3-dinitroimidazolidine-2-carboxylic acid (**1**).

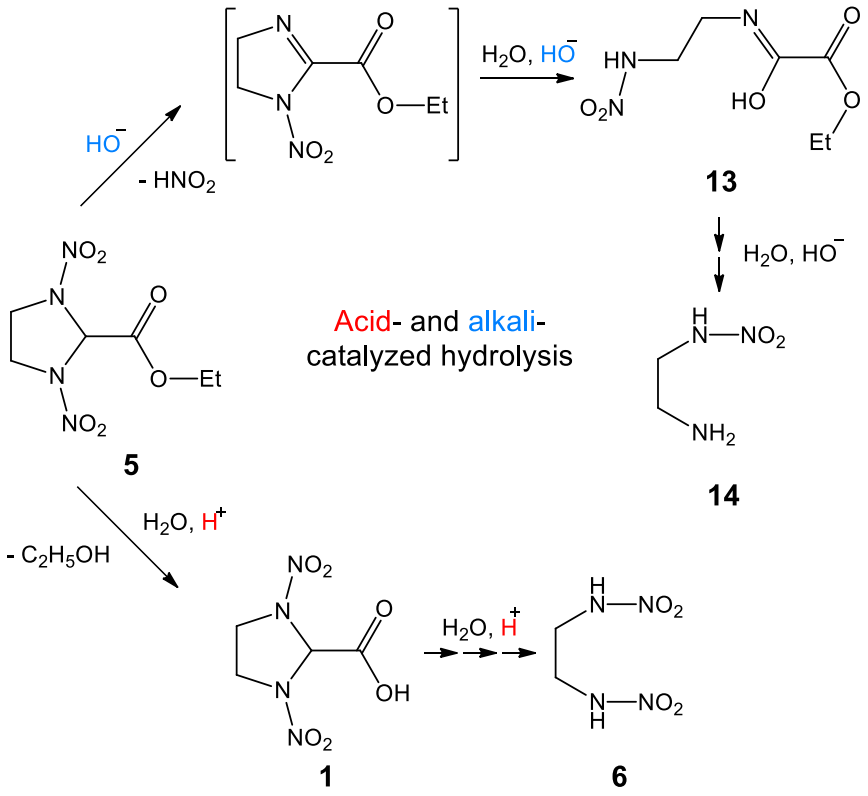
The synthetic procedure for α,α-dinitraminocarboxylic acid is general. For instance, the reaction carried out in this study between N-methylsulfamic acid (**10**) and ester **2** afforded a linear condensation product, ethyl 2,2-bis(methylnitroamino)acetate (**11**) (Scheme 5). Ester **12**, whose isolation was not performed, was likely to be a reaction intermediate.



Scheme 5. Synthesis of ethyl 2,2-bis(methylnitroamino)acetate (**11**).

Due to the α-proton mobility, ester **5** was found to undergo acid- and alkali-catalyzed hydrolyses to open the 1,3-diazacyclopentane ring. For instance, nitrous acid was observed to detach under harsh alkaline hydrolysis conditions with subsequent ring-opening and formation of 2-ethoxy-N-(2-nitroamino)ethyl-2-oxoacetimidic acid (**13**) which underwent hydrolysis through to mononitro ethylenediamine (**14**) (Scheme 6).

At the same time, acid-catalyzed hydrolysis of **5** proceeded to compound **6** (Scheme 6). By varying the reaction parameters (temperature, pH and time), it is possible to halt the acid-catalyzed hydrolysis as soon as acid **1** is formed.



Scheme 6. Acid- and alkali-catalyzed hydrolyses of ethyl 1,3-dinitro-imidazolidine-2-carboxylate (**5**).

The ability of acid **1** to engage in the Curtius and Schmidt rearrangements was examined. The Schmidt rearrangement with either ester **5** or free acid **1** did not bring about the amine group because the initial product underwent denitration under the experimental conditions (100–120% H_2SO_4 concentration). At a lower acid concentration of 80–100%, the initial compound would return unchanged. The low stability of acid **1** was likely due to the high mobility of the α-proton.

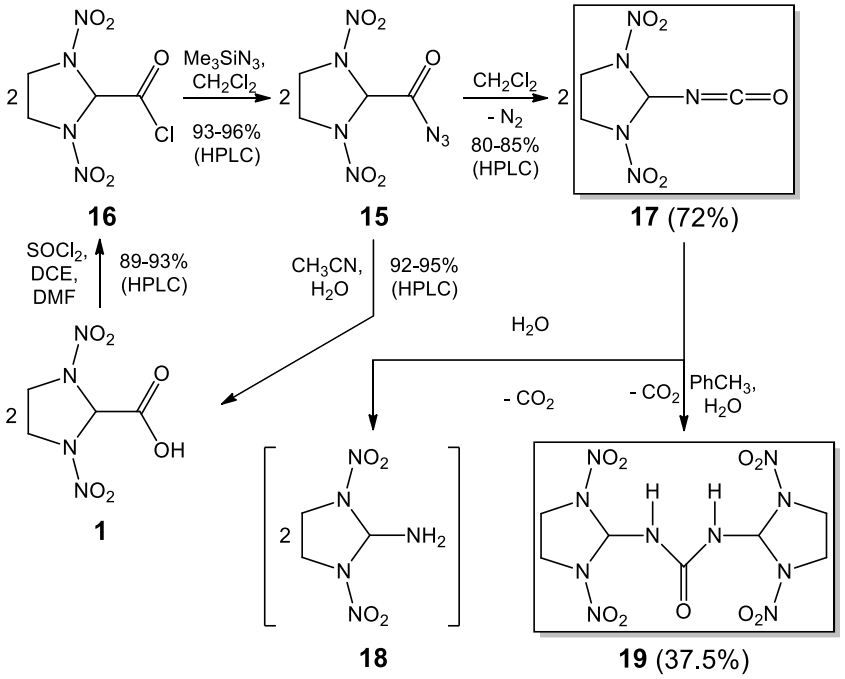
The Curtius rearrangement in a neutral medium requires that 1,3-dinitroimidazolidine-2-carbonyl azide (**15**) be preliminary prepared (Schemes 7 and 8). The azide synthesis via nitrosation of the corresponding hydrazine is impeded by the difficulty preparing hydrazide because of the α-proton mobility in the ester. Another synthesis method of the azide is reacting sodium azide with 1,3-dinitroimidazolidine-2-carbonyl

chloride (**16**) (Scheme 7). However, we could not manage to obtain the corresponding acyl azide by reaction of the acid with sodium azide. This was probably attributed to the high basicity of the salt. Replacing the azidating agent by trimethylsilyl azide (Me_3SiN_3) afforded acyl azide **15**. Chloride **16** was derived by chlorination of acid **1** with thionyl chloride ($SOCl_2$) in the presence of dichloroethane (DCE) and dimethylformamide (DMF) upon heating (89–93% yield as per HPLC). Azidation of chloride **16** to acyl azide **15** was effected in methylene chloride (CH_2Cl_2) (93–96% yield as per HPLC). It is interesting to note that the formed acyl azide **15** was easily hydrolyzed with water. Holding acyl azide **15** in 65% aqueous acetonitrile (CH_3CN) at 0–5°C for 60 h resulted in acid **1** (92–95% yield as per HPLC). When the hydrolysis temperature was raised to room temperature, the yield of acid **1** dropped to 55–60% to form byproducts, including 2-isocyanato-1,3-dinitroimidazolidine (**17**) whose yield reached 6–7% (HPLC) (Scheme 7). In both cases, the partial destruction of acyl azide **15** to nitramine **6** was observed. The Curtius rearrangement of isocyanate **17** was examined in aqueous HCl, toluene, CH_2Cl_2, *tert*-butanol, and acetonitrile.

Acyl azide **15** and isocyanate **17** were found to be instable in polar solvents and to decompose to nitramine **6**. The stability of these compounds was rising in acidic medium. Holding acyl azide **15** in *tert*-butyl alcohol at 80°C for 16 h led to complete decomposition of the starting compound to nitramine **6**. The easy hydrolysis of acyl azide **15** and the poor stability of isocyanate **17** impeded the synthesis of amine **18** (Scheme 7). The Curtius rearrangement of isocyanate **17** was carried out under argon in anhydrous methylene chloride upon boiling (80–85% yield as per HPLC). The hydrolysis of isocyanate **17** was studied either in aqueous HCl, aqueous trifluoroacetic acid (CF_3COOH), mixed $HCl/H_2O/THF$, mixed HCl/H_2O/dioxane, mixed $HCl/H_2O/CH_3CN$ or mixed $CF_3COOH/H_2O/CH_2Cl_2$, and in

mixed THF/H_2O, mixed CH_3CN/H_2O, mixed dioxane/H_2O, mixed dioxane/H_2O/$NaHCO_3$ or mixed dioxane/H_2O/K_2CO_3. The hydrolysis was also examined in heterophase systems based on CH_2Cl_2 or chloroform and HCl with different concentrations. The alkaline hydrolysis was found to rapidly degrade isocyanate **17** to nitramine **6** even at pH 8 (aqueous sodium bicarbonate). In neutral and acidic media in polar solvents, the process proceeded slowly and also resulted in the decomposition of isocyanate **17**. We could not manage to find conditions that would allow the hydrolysis of isocyanate **17** to amine **18**.

The Curtius rearrangement of acyl azide **15** in nonpolar aprotic solvents in the presence of moisture furnished 1,3-bis(1,3-dinitroimidazolidin-2-yl)urea (**19**) (Scheme 7). The formation of this compound corroborates indirectly the synthesis of **18**. Urea **19** was obtained at 75–80°C in toluene (37.5% yield as per HPLC) and in boiling methylene chloride (33.2% yield as per HPLC). This compound was formed by the reaction between isocyanate **17** and amine **18**.



Scheme 7. Synthesis of 1,3-dinitroimidazolidine-2-amine (**18**) and 1,3-bis(1,3-dinitroimidazolidin-2-yl)urea (**19**).

We could not find any mentions of the synthesis of isocyanate **17**, urea **19** or other compounds that comprise structurally the N,N'-(isocyanatomethylene)dinitramide or 1,3-bis[bis(nitroamino)methyl]urea moiety.

Conclusion

In summary, a synthetic strategy for the three new classes of energy-rich compounds, namely carboxymethylnitramines, isocyanatomethylnitramines and sym-dinitraminomethylureas, has been suggested in this study. It was found that α,α-dinitraminocarboxylic acid (and its derivatives) have poor stability in alkaline medium, hindering the Schmidt rearrangement. Transformation of the carboxyl group of α,α-dinitraminocarboxylic acid into the isocyanate group via the Curtius rearrangement has been conducted for the first time. The hydrolysis of 2-isocyanato-1,3-dinitroimidazolidine was examined. In our view, the synthetic methods suggested herein for carboxymethylnitramines, isocyanatomethylnitramines and *sym*-dinitraminomethylureas have a great synthetic potential and offer a broad spectrum of directions in the synthesis of promising energy-rich materials such as strained cyclic, polycyclic and caged nitramines with different structures, and high-energy polymeric compounds.

Experimental

General

Commercially available compounds were used without further purification, unless otherwise stated. Melting points were determined on a Stuart SMP30 melting point apparatus (Bibby Scientific Ltd, UK). Infrared (IR) spectra were recorded on a Simex FT-801 Fourier transform infrared spectrometer in KBr pellets. ^{1}H and ^{13}C NMR

spectra were recorded on a Bruker AV-400 instrument (Bruker Corporation, USA) at 400 MHz and 100 MHz, respectively. Chemical shifts are expressed in ppm (δ). NMR signals were referenced to solvent signal (DMSO-d6, acetone-d6, $CDCl_3$ and D_2O). Elemental analysis was performed on a ThermoFisher FlashEA 1112 elemental analyzer (ThermoFisher, USA). For preparative chromatography, silica gel Kieselgel 60 (0.063–0.2 mm, Macherey-Nagel GmbH & Co. KG, Germany) was used.

The work was done on equipment of the Biysk Regional Center for Shared Use of Scientific Equipment of the SB RAS (Biysk, IPCET SB RAS).

Synthetic procedures

Synthesis of ethyl 1,3-dinitro-1,3-diazacyclopentane-2-carboxylate (5)

Method A. A mixture of **3** (2.96 g, 0.01 mol) with 2 (1.02 g, 0.01 mol) and water (10 mL) was brought to pH = 3.4 (with HCl) and stirred for 3 h at 45–50°C. Upon completion, ethanol (20 mL) was added to the reaction mass upon stirring, and the resultant suspension was filtered. The crystalline precipitate was successively washed with ethanol and ether, and then air-dried for 2 h. Afterwards, while stirring and maintaining the temperature between -30 to -35°C, the resultant precipitate was put into nitric acid (50 g, 98% content) and held for 3 h at the same temperature with stirring. Upon completion, the reaction mass was diluted with ice water and extracted with chloroform. The extract was successively washed with water, 2% sodium bicarbonate solution, water, and dried over $MgSO_4$. The solvent was then withdrawn from the extract *in vacuo* to furnish compound **5** (0.4 g, 95.1% content) as a yellow viscous liquid. Yield: 0.38 g, 1.624 mmol (16.3% calculated as compound **3**). Anal. Calcd for $C_6H_{10}N_4O_6$: C, 30.77; H, 4.30; N, 23.93. Found: C, 30.67; H, 4.31; N, 24.05. IR (KBr): v = 1550 (N-NO_2), 1755 (C=O) cm^{-1}. ^1H NMR (acetone-d6): δ = 1.32 (3H, t),

4.26 (2H, q), 4.34 (2H, q), 4.51–4.61 (2H, m), 6.53 (1H, s) ppm. $^{13}C\{1H\}$ NMR (acetone-d6): δ = 13.3, 48.5, 62.9, 74.5, 164.8 ppm.

Method B. To a solution of **6** (1.50 g, 0.01 mol) in concentrated H_2SO_4 (20 mL) was added dropwise **2** (1.02 g, 0.01 mol) at 0–5°C with stirring. Afterwards, keeping stirring and maintaining the same temperature, the reaction mass was held for 5 min and diluted with ice water. The resultant mixture was extracted with chloroform. The extract was successively washed with water, 2% sodium bicarbonate solution, water, and dried over $MgSO_4$. The solvent was then removed from the extract *in vacuo* to yield compound **5** (0.35 g, 94.6% content) as a yellow viscous liquid. Yield: 0.33 g, 1.414 mmol (14.1% calculated as compound **6**).

Method C. A solution of **2** (10.17 g, 0.1 mol) in water (17.6 mL) was added to a mixture of **7** (6 g, 0.1 mol) with water (20 mL) and acetic acid (5.8 mL) at 0°C for 30 min with stirring. Afterwards, keeping stirring and maintaining the same temperature, the reaction mass was held for 1 h. While stirring and maintaining the same temperature, to the mixture was successively added portionwise sodium nitrite (15.2 g, 0.22 mol) for 10 min and acetic acid (5.6 mL) for 30–40 min at -5–0°C. Then, keeping stirring and maintaining the same temperature, the reaction mass was held for 40 min, diluted with water (60 mL), and extracted with ethyl acetate (3 x 15 mL, HPLC monitoring). The extract was washed with water and a saturated sodium chloride solution, and dried over calcined $MgSO_4$. The solvent was then removed from the extract *in vacuo* to afford compound **8** (10.94 g, 93.5% content) as an unstable orange liquid. Yield: 10.23 g, 50.595 mmol (50.7% calculated as initial ethylenediamine). IR (KBr): ν = 1449 (N-NO), 1747 (C=O) cm^{-1}. Anal. Calcd for $C_6H_{10}N_4O_4$: C, 35.65; H, 4.99; N, 27.71. Found: C, 35.70; H, 5.03; N, 27.74. It was impossible to interpret the NMR spectrum of **8** due to its instability and likely inability

to generate resonance structures. The ^{1}H and $^{13}C\{1H\}$ NMR spectra taken in acetone-d6 for the newly prepared compound are furnished in the SI.

Nitration of **8** to **5** could be carried out in HNO_3 mixed with either trifluoroacetic or nitric anhydride.

Compound **8** (10.5 g, 93.5% content, 0.048 mol) in dichloromethane (20 mL) was added dropwise to a mixture of trifluoroacetic anhydride (30 mL) and nitric acid (30 mL, 99.8% content) for 30 min at between -18 and -15°C with stirring. Afterwards, the reaction mass was stirred for 40 min at the same temperature, diluted with excess ice water, and extracted with chloroform (4 x 15 mL). The extract was successively washed with 2% sodium carbonate solution and water, and then dried over $MgSO_4$. The solvent was withdrawn from the extract *in vacuo* to deliver **5** (11.3 g, 96% content) as a yellow viscous liquid. Yield: 10.85 g, 46.325 mmol (95.4% calculated as compound **8**).

To a mixture of nitric anhydride (30 g) with nitric acid (70 mL, 99.8% content) was added dropwise **8** (16 g, 93.5% content, 0.074 mol) in dichloromethane (20 mL) at between -30 and -35°C with stirring. After that, keeping stirring and maintaining the same temperature, the reaction mass was held for 20 min and heated to 20–25°C to eliminate nitrogen oxides by bubbling nitrogen through the reaction mixture. After bubbling was completed, the whole was diluted with ice water and extracted with chloroform. The extract was successively washed with water, 2% sodium carbonate solution and water, and then dried over $MgSO_4$. The solvent was withdrawn from the extract *in vacuo* to give **5** (12.5 g, 94% content) as a yellow viscous liquid. Yield: 11.75 g, 50.177 mmol (67.8% calculated as compound **8**).

Nitration of ethyl 1,3-dinitroso-1,3-diazacyclopentane-2-carboxylate (8) to 1-nitroso-3-nitro-1,3-diazacyclopentane-2-carboxylate (9)

To a solution of **8** (4.5 g, 93.5% content, 0.02 mol) in dichloromethane (5 mL) was added portionwise nitric acid (30 mL, 99.8% content) at between -35 and -30°C with stirring. Then, keeping stirring and maintaining the same temperature, the reaction mass was held for 15 min, diluted with ice water, and extracted with chloroform. The extract was successively washed with water, 2% sodium carbonate solution and water, and dried over $MgSO_4$. The solvent was withdrawn from the extract *in vacuo* to give **9** (3.2 g, 96.3% content) as an unstable, orange thin liquid. Yield: 3.08 g, 14.125 mmol (67.8% calculated as compound **8**). Anal. Calcd for $C_6H_{10}N_4O_5$: C, 33.03; H, 4.26; N, 25.68. Found: C, 33.21; H, 4.31; N, 25.53. IR (KBr): v = 1554 (N-NO_2), 1749 (C=O) cm^{-1}. ^1H NMR (acetone-d6): δ = 1.27 (3H, q), 3.83–5.18 (6H, m), 5.88, 6.27 and 6.93 (1H, three s) ppm. $^{13}C\{1H\}$ NMR (acetone-d6): δ = 14.0, 43.8, 47.8, 48.1, 49.2, 63.3, 63.9,72.5, 75.2, 164.5, 165.9 ppm.

The signal splitting in the NMR spectra probably occurs due to the ability of the compound to form resonance structures and generate two conformers issued from the *syn* and *anti*-orientations of the nitroso group.

Synthesis of ethyl 2,2-bis(methylnitroamino)acetate (11)

To a solution of **10** (5.55 g, 0.05 mol) in sulfuric acid (30 mL) was added dropwise **2** (2.55 g, 0.025 mol) at 5–10°C with stirring. Keeping stirring and maintaining the same temperature, the reaction mass was held for 10 min, nitric acid (5 mL) was added, and the whole was held for another 2–3 min. Upon completion, the reaction mixture was diluted with ice water and extracted with chloroform. The extract was successively washed with water, 2% sodium carbonate solution and water, and dried over $MgSO_4$. The solvent was next removed from the extract *in vacuo* to furnish **11**

(0.8 g, 95% content) as a yellow thin liquid. Yield: 0.76 g, 3.218 mmol (12.9% calculated as compound **10**). Anal. Calcd for $C_6H_{12}N_4O_6$: C, 30.51; H, 5.12; N, 23.72. Found: C, 30.59; H, 5.17; N, 23.80. ^{1}H NMR (acetone-d6): δ = 1.27 (3H, t), 3.97 (6H, s), 4.31 (2H, q), 6.53 (1H, s) ppm. ^{13}C{1H} NMR (acetone-d6): δ = 14.1, 39.2, 64.0, 74.8, 163.1 ppm.

Alkali-catalyzed hydrolysis of ethyl 1,3-dinitro-1,3-diazacyclopentane-2-carboxylate (5) to ethyl 2-ethoxy-N-(2-nitroamino)ethyl-2-oxoacetimidic acid (13) and mononitro ethylenediamine (14)

To a solution of **5** (2.34 g, 0.01 mol) in methanol (20 mL) was added portionwise a potassium hydroxide solution (0.56 g, 0.01 mol) in methanol (50 mL) with stirring. The reaction mixture was then stirred for 10 min at room temperature, treated with HCl, and the precipitated potassium chloride was discarded. The filtrate was evaporated *in vacuo*. The residue was diluted with acetone, filtered, and dried at room temperature until constant weight to afford hydrochloric **14** as a colorless crystalline solid. Yield: 0.5 g, 3.532 mmol (35.3% calculated as **5**). Mp = 169–171°C. Anal. Calcd for $C_2H_8N_3ClO_2$: C, 16.97; H, 5.70; N, 29.68. Found: C, 17.06; H, 5.63; N, 29.57. IR (KBr): v = 3000 (NH_3^+), 1590(NH_3^+), 1565 (N-NO_2) cm^{-1}. ^{1}H NMR (D_2O, standard DSS): δ = 3.32 (2H, t), 3.88 (2H, t) ppm. ^{13}C{1H} NMR (D_2O): δ = 37.7, 42.8 ppm.

The filtrate was evaporated and treated with 2-propanol. The resultant precipitate was collected by filtration, washed with 2-propanol, and recrystallized from acetone to yield **13** as a white crystalline powder. Yield: 0.18 g, 0.877 mmol (8.8% calculated as compound **5**). Mp = 121–122°C. Anal. Calcd for $C_6H_{11}N_3O_5$: C, 34.12; H, 5.21; N, 22.75. Found: C, 34.05; H, 5.28; N, 22.80. IR (KBr): v = 3370 (OH), 3240 (NH), 1730 (C=O), 1560 (N-NO_2) cm^{-1}. ^{1}H NMR (DMSO-d6): δ = 1.27 (3H, t) 4.23 (2H, q), 3.33

and 3.51 (4H, two t), 9.00 (1H, t), 11.98 (1H, s) ppm. $^{13}C\{1H\}$ NMR (DMSO-d6): δ = 13.9, 36.5, 43.9, 62.1, 157.2, 160.4 ppm.

Acid-catalyzed hydrolysis of ethyl 1,3-dinitro-1,3-diazacyclopentane-2-carboxylate (5) to 1,3-dinitro-1,3-diazacyclopentane-2-carboxylic acid (1)

Compound **5** (10.37 g, 96% content, 0.042 mol) was boiled in concentrated HCl (50 mL) for 5–6 h (HPLC control). After the whole ester had reacted, the mixture was evaporated in vacuo to 20–25% of the initial volume and held at 2–4°C for 2 days. The precipitate was collected by filtration, washed with concentrated HCl, and dried at room temperature until constant weight to give **1** as a white crystalline powder. Yield: 6 g, 29.110 mmol (68.5% calculated as compound **5**). Mp = 141–144°C. Anal. Calcd for $C_4H_6N_4O_6$: C, 23.31; H, 2.93; N, 27.18. Found: C, 23.44; H, 3.02; N, 27.20. IR (KBr): v = 1748(C=O), 1551 (N-NO_2) cm^{-1}. ^1H NMR (acetone-d6): δ = 4.21–4.30 (2H, m), 4.52–4.62 (2H, m), 6.55 (1H, s), 7.44 (1H, s) ppm. $^{13}C\{1H\}$ NMR (acetone-d6): δ = 48.5, 74.6, 165.5 ppm.

Synthesis of 2-isocyanato-1,3-dinitroimidazolidine (17)

Acid **1** (0.5 g, 2.42 mmol), DMF (0.05 g), DCE (0.6 mL) and thionyl chloride (1 mL, 13.78 mmol) were mixed and the suspension was then stirred at 50°C until fully dissolved. After the acid was dissolved completely, the mixture was stirred another 20 min at 50°C. After that, the resultant reaction mass was evaporated to dryness in vacuo at 35°C to furnish a yellow resin (89–93% yield of chloride **16** as per HPLC). The flask was then evacuated with argon, whereupon the resultant chloride **16** was dissolved in anhydrous methylene chloride (9 mL). Trimethylsilyl azide (1.1 mL, 8.36 mmol) was then weighed into the reaction mass with stirring at -20°C for 3–4 min. The resultant mixture was stirred at between -20 and -15°C for 1 h (93–96%

yield of acyl azide **15** as per HPLC). After that, the reaction mass was heated to boil and held for 6 h with stirring. The resultant mixture was then evaporated to dryness in a rotary evaporator to give a brown resin (0.51 g) containing compound **17** (70%, HPLC). Yield: 0.36 g, 1.758 mmol (72% calculated as acid **1**).

The compound in the pure form was isolated in two steps. At first, the compound was purified by preparative chromatography. A mixture of chloroform/acetone in a volume ratio of 5:1 (Rf = 0.47) was used as the eluent. The solution after preparative chromatography was evaporated at 20°C and extracted with anhydrous chloroform (to remove nitramine **6** as impurity). Chloroform was evaporated at 20°C to furnish isocyanate **17** as a colorless resin that cured over time (96% content as per HPLC). Anal. Calcd for $C_4H_5N_5O_5$: C, 23.65; H, 2.48; N, 34.48. Found: C, 23.96; H, 2.55; N, 34.53. IR (KBr): v = 2921, 2850, 2212 (N=C=O), 2159 (N=C=O), 1713 (C=O), 1555 (N-NO_2), 1543 (N-NO_2), 1368, 1294, 1276, 1198, 1096, 1004, 904, 857, 805, 762, 735, 676, 630 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.36 (4H, s), 6.96 (1H, d) ppm. $^{13}C\{1H\}$ NMR ($CDCl^3$): δ = 47.4, 77.7, 156.0 ppm.

Synthesis of 1,3-di-(1,3-dinitro-1,3-diazacyclopentyl-2)urea (19)

Acid **1** (10.4 g, 0.05 mol), DMF (1.04 g), DCE (12,5 mL) and thionyl chloride (20,8 mL, 0.28 mol) were mixed, and the suspension was then stirred at 50°C until fully dissolved. After the acid had completely dissolved, the mixture was stirred another 20 min at 50°C. After that, the reaction mass was evaporated to dryness *in vacuo* at 35°C. The residue was dissolved in toluene (200 mL), and trimethylsilyl azide (7.5 g, 0.06 mol) was added at -20°C with stirring for 5–6 min. The resultant mixture was stirred at between -20 and -15°C for 1 h. The whole was then heated to 75°C and held for 3 h. The solvent was next removed from the resultant solution *in vacuo*. The residue was treated with methylene chloride and collected by filtration.

The precipitate was recrystallized from methanol to give **19** as a white crystalline powder. Yield: 3.6 g, 9.468 mmol (37.5% calculated as compound **5**). Some of the product remained in the mother solution after crystallization. Mp = 220–221°C. Anal. Calcd for $C_7H_{12}N_{10}O_9$: C, 22.11; H, 3.18; N, 36.84. Found: C, 22.20; H, 3.25; N, 36.77. IR (KBr): v = 3128 (NH), 2888, 2771, 1758 (C=O), 1733 (C=O), 1557 (N-NO_2), 1536 (N-NO_2), 1411, 1362, 1289, 1199, 1152, 1074, 993, 920, 821, 761, 736, 652 cm^{-1}. ^{1}H NMR (acetone-d6): δ = 4.43 and 4.69 (8H, two m), 8.04 (2H, s), 13.52 (2H, br s) ppm. ^{13}C{1H} NMR (acetone-d6): δ = 48.1, 79.8, 149.7 ppm.

Supporting Information

Supporting Information File 1 [Pdf]: ^{1}H and ^{13}C NMR for all new compounds.

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