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Synthesis and spectra of some ^{2}H-, ^{13}C-, and ^{15}N-labeled isomers of 1,3,3-trinitroazetidine and 3,3-dinitroazetidinium nitrate

M. D. Coburn[a]; M. A. Hiskey[a]; J. C. Oxlcy[b]; J. L. Smith[b]; W. Zheng[b]; E. Rogers[b]
[a] Los Alamos National Laboratory, University of California, Los Alamos, NM [b] University of Rhode Island, Kingston, RI

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SYNTHESIS AND SPECTRA OF SOME ^{2}H-, ^{13}C-, and ^{15}N-LABELED ISOMERS OF 1,3,3-TRINITROAZETIDINE AND 3,3-DINITROAZETIDINIUM NITRATE

Michael D. Coburn and Michael A. Hiskey
University of California, Los Alamos National Laboratory
Los Alamos, NM 87545

Jimmie C. Oxley, James L. Smith, Weiyi Zheng, and Evan Rogers
University of Rhode Island
Kingston, RI 02881

ABSTRACT

The title compounds were synthesized by utilizing appropriately labeled starting materials and reagents according to literature procedures.[1,2] The products were characterized by NMR and mass spectral analysis. Unequivocal assignments of all NMR chemical shifts of the unlabeled title compounds and their intermediate precursors were facilitated by the NMR spectra of the labeled compounds along with carbon-hydrogen correlation experiments.

INTRODUCTION

The original synthesis of 1,3,3-trinitroazetidine (TNAZ) was reported in 1990;[3] however, the recent development and scale-up of a new, more economical process[1] has made this material a viable candidate for some melt-cast explosive applications that require performance greater than that of existing TNT-based explosives. Our ongoing study of the thermal decomposition mechanisms of

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energetic materials required the synthesis of certain ^{2}H-, ^{13}C-, and ^{15}N-labeled isomers of TNAZ and 3,3-dinitroazetidinium nitrate, a new high-performance, water soluble explosive.[2]

DISCUSSION

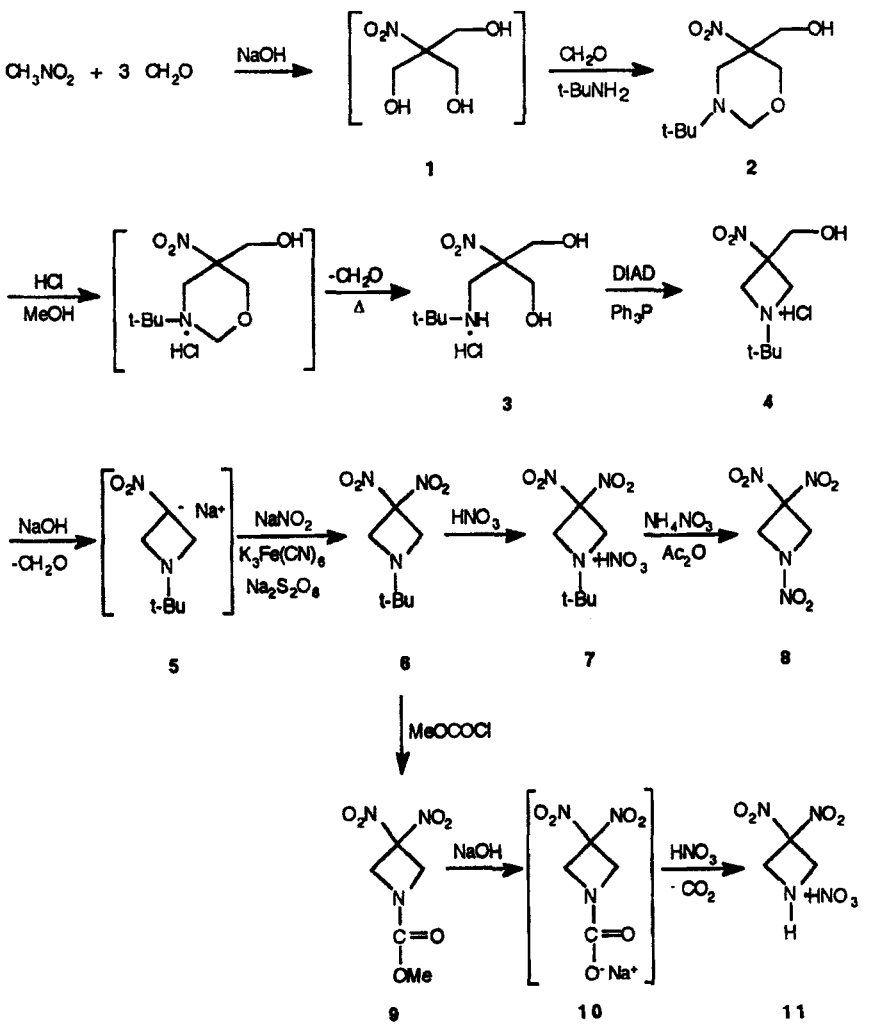
Synthesis

The synthesis routes to the title compounds were adapted from literature procedures[1,2] (SCHEME 1). Thus, formaldehyde was treated with nitromethane in the presence of a catalytic amount of sodium hydroxide to give a solution of tris(hydroxymethyl)nitromethane (**1**), which reacted with t-butylamine and another molecule of formaldehyde to yield 3-t-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine (**2**). Addition of **2** to a stoichiometric amount of hydrochloric acid in methanol effected cleavage of the ring with elimination of formaldehyde to give 2-t-butylaminomethyl-2-nitro-1,3-propanediol hydrochloride (**3**). The Mitsunobu reaction of **3** with di-i-propyl azodicarboxylate (DIAD) and triphenylphosphine (TPP) in 2-butanone provided 1-t-butyl-3-hydroxymethyl-3-nitroazetidine hydrochloride (**4**). Treatment of a solution of **4** with sodium hydroxide neutralized the hydrochloric acid and deformylated the molecule to produce a solution of the sodium salt of 1-t-butyl-3-nitroazetidine (**5**), which was oxidatively nitrated with sodium nitrite, potassium ferricyanide, and sodium persulfate to 1-t-butyl-3,3-dinitroazetidine (**6**), a common intermediate to both title compounds. Nitrolysis of 1-t-butyl-3,3-dinitroazetidinium nitrate (**7**) with ammonium nitrate in acetic anhydride gave 1,3,3-trinitroazetidine (TNAZ) (**8**). Methyl chloroformate reacted with **6** to produce 1-methoxycarbonyl-3,3-dinitroazetidine (**9**), which was easily saponified to a solution of sodium 3,3-dinitroazetidine-1-carboxylate (**10**).

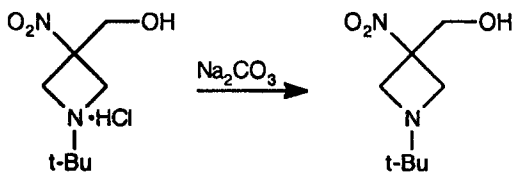
Treatment of **10** with nitric acid caused immediate decarboxylation to give 3,3-dinitroazetidinium nitrate (**11**). Although unnecessary in the synthesis of **8** and

SCHEME 1

Synthesis of 1,3,3-Trinitroazetidine and 3,3-Dinitroazetidinium Nitrate



11, a sample of 1-t-butyl-3-hydroxymethyl-3-nitroazetidine (**12**) was obtained for NMR studies by treatment of **4** with an equivalent amount of sodium carbonate.



4 **12**

The use of formaldehyde-d_2 and deuterated solvents in the reactions of SCHEME 1 produced isolated quantities of 3-t-butyl-5-hydroxymethyl-d_3-5-nitrotetrahydro-1,3-oxazine-d_6 (**2a**), 2-t-butylamino-*d*-methyl-d_2-nitro-1,3-propanediol-d_6 deuteriochloride (**3a**), 1-t-butyl-3-hydroxymethyl-d_3-3-nitroazetidine-d_4 deuteriochloride (**4a**), 1-t-butyl-3,3-dinitroazetidine-d_4 (**6a**), 1-t-butyl-3,3-dinitroazetidinium-d_4 nitrate (**7a**), 1,3,3-trinitroazetidine-d_4 (**8a**), 1-methoxycarbonyl-3,3-dinitroazetidine-d_4 (**9a**), and 3,3-dinitroazetidinium-d_6 nitrate (**11a**). The formation of **2a** was found to be much slower than that of **2**, but the yield was good. However, the deuterium isotope effect not only slowed the deformylative cleavage of the hydrochloride of **2a**, but enhanced decomposition side-reactions to result in a much lower yield of **3a** than that obtained for **3**. The yields of **4a**, **6a**, and **8a** were comparable to those obtained for **4**, **6**, and **8**; however, the yields of **9a** and **11a** were much lower than those obtained for **9** and **11**.

By starting with nitromethane-^{13}C, 3-t-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine-5-^{13}C (**2b**), 2-t-butylaminomethyl-2-nitro-1,3-propanediol-2-^{13}C hydrochloride (**3b**), 1-t-butyl-3-hydroxymethyl-3-nitroazetidine-3-^{13}C hydrochloride (**4b**), and 1-t-butyl-3,3-dinitroazetidine-3-^{13}C (**6b**) were

produced in good yields. Treatment of **6b** with nitric acid and nitric-^{15}N acid produced 1-t-butyl-3,3-dinitroazetidinium-3-^{13}C nitrate (**7b**) and 1-t-butyl-3,3-dinitroazetidinium-3-^{13}C nitrate-^{15}N (**7c**), respectively. Nitrolysis of **7b** with ammonium nitrate in acetic anhydride gave 1,3,3-trinitroazetidine-3-^{13}C (**8b**) in good yield. Similar treatment of **7c** with ammonium nitrate-^{15}N in acetic anhydride gave a good yield of 3,3-dinitro-1-nitro-^{15}N-azetidine-3-^{13}C (**8c**). Conversion of **6b** to 1-methoxycarbonyl-3,3-dinitroazetidine-3-^{13}C (**9b**) and that of **9b** to 3,3-dinitroazetidinium-3-^{13}C nitrate-^{15}N (**11b**) were accomplished in fair yields.

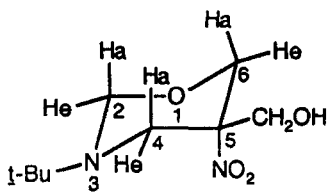
When nitromethane-^{15}N was employed, 3-t-butyl-5-hydroxymethyl-5-nitro-^{15}N-tetrahydro-1,3-oxazine (**2c**), 2-t-butylaminomethyl-2-nitro-^{15}N-1,3-propanediol hydrochloride (**3c**), and 1-t-butyl-3-hydroxymethyl-3-nitro-^{15}N-azetidine hydrochloride (**4c**) were obtained in good yields. Deformylation of **4c** followed by oxidative nitration using sodium nitrite-^{15}N produced a fair yield 1-t-butyl-3,3-dinitro-$^{15}N_2$-azetidine (**6c**), which was treated with nitric-^{15}N acid to give 1-t-butyl-3,3-dinitro-$^{15}N_2$-azetidinium nitrate-^{15}N (**7d**). Nitrolysis of **7d** with ammonium nitrate-^{15}N in acetic anhydride gave 1,3,3-trinitro-$^{15}N_3$-azetidine (**8d**) in good yield. Treatment of **6c** with methyl chloroformate gave a good yield to 1-methoxycarbonyl-3,3-dinitro-$^{15}N_2$-azetidine (**9c**), which was converted to 3,3-dinitro-$^{15}N_2$-azetidinium nitrate-^{15}N (**11c**) in fair yield.

Deformylation of **4** followed by oxidative nitration using sodium nitrite-^{15}N produced 1-t-butyl-3,3-dinitro-$^{15}N_1$-azetidine (**6d**), which was treated with nitric acid and nitric-^{15}N acid to give 1-t-butyl-3,3-dinitro-$^{15}N_1$-azetidinium nitrate (**7e**) and 1-t-butyl-3,3-dinitro-$^{15}N_1$-azetidinium nitrate-^{15}N (**7f**), respectively. Nitrolysis of **7e** with ammonium nitrate in acetic anhydride gave 3,3-dinitro-$^{15}N_1$-1-nitroazetidine (**8e**) in good yield. Similarly, a good yield of 3,3-dinitro-$^{15}N_1$-1-

nitro-^{15}N-azetidine (**8f**) was obtained by nitrolysis of **7f** with ammonium nitrate-^{15}N in acetic anhydride. Treatment of **6d** with methyl chloroformate gave a good yield of 1-methoxycarbonyl-3,3-dinitro-$^{15}N_1$-azetidine (**9d**), which was converted to 3,3-dinitro-$^{15}N_1$-azetidinium nitrate (**11d**) in fair yield. Treatment of **6** with nitric-^{15}N acid gave 1-t-butyl-3,3-dinitroazetidinium nitrate-^{15}N (**7g**), which was nitrolyzed with ammonium nitrate-^{15}N in acetic anhydride to 3,3-dinitro-1-nitro-^{15}N-azetidine (**8g**).

NMR Spectra

The ^{1}H-NMR spectrum of **2** is very complex in that all the ring protons are non-equivalent because the t-butyl group freezes the compound in a single chair conformation, as shown below. Dipole moment measurements of a series of substituted 5-nitrotetrahydro-1,3-oxazines, including 3-t-butyl-5-methyl-5-nitrotetrahydro-1,3-oxazine, compared with calculated values indicate that the nitro group is axial in every example.[4]

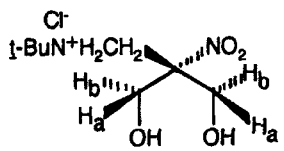


2

The spectra of the labeled compounds **2a-c** in conjunction with a carbon-hydrogen correlation study and the gem-^{1}H coupling constants have allowed unequivocal assignment of all the ^{1}H and ^{13}C chemical shifts (TABLE 1). The ^{13}C-NMR spectrum of **2a** shows that the shifts at 26.1 ppm and 52.2 ppm, which are not coupled to ^{2}H, are from the t-butyl carbons. In the ^{13}C-NMR spectrum of **2b**, the

^{13}C-labeled carbon-5 (89.2 ppm) couples with the hydroxymethyl carbon (63.9 ppm, 38 Hz), carbon-4 (48.6 ppm, 39 Hz), and carbon-6 (67.9 ppm, 40 Hz), but not carbon-2 (80.7 ppm). Surprisingly, the central t-butyl carbon of **2b** at 52.2 ppm was also split by the 5-^{13}C (3 Hz). The assignment of the 48.6 ppm shift to carbon-4 is based upon the similarity of this shift to other methylene carbons between a protonated t-butylamino group and carbon substituted with nitro and hydroxymethyl groups, such as **3** (43.7 ppm) and **4** (53.3 ppm). In addition, carbon-6 would be expected to be deshielded more by its adjacent oxygen than carbon-4 by its adjacent nitrogen. As expected, the nitro-^{15}N in **2c** couples with carbon-5. However, the observations that the ^{13}C-labeled carbon-5 in **2b** couples only with the equatorial proton at 3.60 ppm on carbon-4 and that the nitro-^{15}N in **2c** couples only with the axial proton at 2.62 ppm on carbon-4 are not understood.

Compound **3**, as illustrated below, is prochiral and thus, the gem protons on the hydroxymethyl groups are non-equivalent and split each other by 12 Hz (TABLE 2).



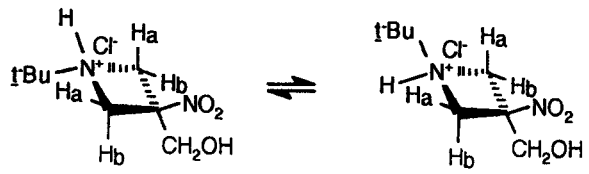
3

As expected, all the methylene carbons in the ^{13}C-NMR spectrum of **3a** were split into pentets and the ^{13}C-labeled carbon-2 of **3b** coupled with all methylene carbons and also the central t-butyl carbon in the ^{13}C-NMR spectrum. The ^{1}H-NMR spectrum of **3b** showed coupling of the ^{13}C-labeled carbon-2 with the t-butylaminomethylene protons at 3.86 ppm (3 Hz) and the hydroxymethyl protons at

4.22 ppm (3 Hz), but not the hydroxymethyl protons at 3.99 ppm. In contrast, the ^{1}H-NMR spectrum of **3c** showed coupling of ^{15}N with the t-butylaminomethylene protons at 3.86 ppm (3 Hz) and the hydroxymethyl protons at 3.99 ppm (4 Hz), but not the hydroxymethyl protons at 4.21 ppm.

The methylene protons of the azetidine ring and the hydroxymethyl group of **4** appear in the ^{1}H-NMR spectrum at 25°C as very broad singlets, but at 80°C the azetidine ring protons become two doublets (J = 12 Hz) and the hydroxymethyl protons are a sharp singlet (TABLE 3). The ^{1}H-NMR spectrum of **4b** at 80°C showed coupling of the ^{13}C-labeled carbon-3 with the hydroxymethylene protons at 4.75 ppm (2 Hz) and the azetidine ring protons at 5.29 ppm (5 Hz), but not the azetidine ring protons at 5.04 ppm. In contrast, the ^{1}H-NMR spectrum of **4c** at 80°C showed coupling of ^{15}N with the hydroxymethylene protons at 4.75 ppm (3 Hz) and the azetidine ring protons at 5.04 ppm (2 Hz), but not the azetidine ring protons at 5.29 ppm. At 25°C, carbon-3 appeared as two distinct broad shifts at 80.2 ppm and 83.1 ppm in the ^{13}C-NMR spectrum of a concentrated solution of **4** and at 80.0 ppm and 82.8 ppm in the ^{13}C-NMR spectrum of a dilute solution of **4b**. At 80°C, the two carbon-3 shifts of **4** and **4b** collapsed to broad singlets at 82.2 ppm and 82.1 ppm, respectively. As a result of the broadness of the carbon-3 shifts, coupling of the nitro-^{15}N with carbon-3 was not observed in the ^{13}C-NMR spectrum of **4c**. Similarly, in the ^{15}N-NMR spectra at 25°C both the azetidine nitrogen and the nitro nitrogen of **4** as well as the nitro nitrogen of **4c** gave two distinct signals, which collapsed to single peaks at 80°C. These results suggest that **4** is an equilibrium mixture of two isomers, one with the t-butyl group on the same side of the ring as the hydroxymethyl group and the other with the t-butyl

group on the same side of the ring as the nitro group.



4

Equilibration would require deprotonation of one species, followed by protonation to give the other isomer, which is sufficiently slow at 25°C to allow detection of both isomers by NMR, but is too fast at 80°C to allow detection of both isomers. The NMR spectra of the free base **12** are qualitatively similar to those of **4** at 80°C.

The NMR-spectra of **6-6d**, **7-7f**, **8-8g**, **9-9d**, and **11-11d** are given in TABLES 4, 5, 6, 7, and 8, respectively. In every instance the ^{1}H-NMR spectra of the 3-^{13}C isomers exhibited coupling of 5 Hz between ^{13}C and the azetidine ring protons and those of the nitro-^{15}N isomers showed coupling of 2-3 Hz between ^{15}N and the ring protons. In addition, the ^{13}C-NMR spectra of the nitro-^{15}N isomers showed coupling between ^{15}N and carbon-3 of 11-14 Hz. As in the spectra of some of its precursors, the ^{13}C-NMR spectrum of **6b** showed coupling between 3-^{13}C and the central t-butyl carbon.

Mass Spectra

Mass spectral analysis of the TNAZ isomers was performed using electron impact (EI) (Table 9) as well as chemical ionization (CI) with methane gas (Table 10). For EI the molecular weight was consistent with the isotopic assignment. For CI the parent P peak was not observed, but fragments representing reactions

with methane (P+1, P+29, P+41) were observed, allowing inference as to the parent mass. Other principal fragments were consistent with loss of nitro and nitroso groups.

EXPERIMENTAL METHOD

All NMR spectra were obtained on a JEOL GSX high resolution Fourier transform spectrometer. Resonance frequencies for ^{1}H, ^{13}C, and ^{15}N were 399.65 MHz, 100.40 MHz, and 40.40 MHz, respectively. All ^{13}C-NMR spectra were obtained with proton decoupling. The ^{15}N-NMR spectra were obtained with single-pulse gated decoupling without nuclear Overhauser enhancement and are relative to and upfield of external nitromethane = 0. TNAZ isotopic purity was assessed using a mass spectrometer (Finnigan-MAT TSQ 700) with a gas chromatographic (GC, Varian 3400) inlet. The GC was equipped with a capillary column (J&W DB-5MS, 30m x 0.25mm i.d.). An acetone solution of the TNAZ (0.02%) was injected (200°C) into the GC at an initial temperature of 80°C; after a one minute hold, the temperature was ramped to 210°C at 7.5°C/min. The transfer line temperature was 200°C. Electron impact ionization (EI) was accomplished using 70eV and 400 uA emission. The ion source was operated at 150°C, and the scan range for EI was 35-400 amu. Chemical ionization (CI) was accomplished using methane gas; solid samples were introduced via a solids probe (25-35°C). Melting points were determined on all solid products and were within 2°C of literature values.

3-t-Butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazines (2-2c)

To a slurry of paraformaldehyde (2.16 g, 0.072 mol) and 40% sodium hydroxide (1 drop) in water (10 ml) was added the appropriate nitromethane (1.0 g,

0.016 mol). The mixture was stirred at 60° for one h, then t-butylamine (1.70 ml, 1.17 g, 0.016 mol) in water (3 ml) was added dropwise at 60°. Solid began to precipitate during the addition. The mixture was held at 60° for 5 h, cooled, and filtered. The solid was washed with water and dried to give the 3-t-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine in the yield reported in TABLE 1. In the case of **2a**, paraformaldehyde-d_2, 40% sodium deutroxide, deuterium oxide, and nitromethane-d_3 were used.

2-t-Butylaminomethyl-2-nitro-1,3-propanediol Hydrochlorides (**3-3c**)

To a solution of concentrated hydrochloric acid (1.0 ml, 0.012 mol) in methanol (20 ml) was added the appropriate 3-t-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine (0.012 mol). The resulting mixture was heated under gentle reflux for 20 h to drive the reaction to completion. The solvent was removed under reduced pressure and the residue was stirred in 2-propanol (20 ml). After the mixture had been chilled in the freezer, the solid was collected by filtration, washed with a little cold 2-propanol, and dried to give the 2-t-butylaminomethyl-2-nitro-1,3-propanediol hydrochloride in the yield reported in TABLE 2. In the case of **3a**, methyl alcohol-*d* and 37% deuterium chloride in deuterium oxide were employed in the reaction.

1-t-Butyl-3-hydroxymethyl-3-nitroazetidine Hydrochlorides (**4-4c**)

To a mixture of the appropriate 2-t-butylaminomethyl-2-nitro-1,3-propanediol hydrochloride (0.01 mol) and di-i-propyl azodicarboxylate (2.22 g, 0.011 mol) in 2-butanone (5 ml) is added dropwise a solution of triphenylphosphine (2.88 g, 0.011 mol) in 2-butanone (2.5 ml) at 50°C. After completed addition the mixture was filtered hot to give a solid, which was washed

with a little 2-butanone and air dried to give the 1-t-butyl-3-hydroxymethyl-3-nitroazetidine hydrochloride in the yield reported in TABLE 3.

1-t-Butyl-3-hydroxymethyl-3-nitroazetidine (**12**)

To a stirred solution of sodium carbonate (2.35g, 0.022 mol) in water (50 ml) was added **4** (5.0 g, 0.022 mol). The resulting mixture was extracted with chloroform (2 x 25 ml) and the combined extracts were dried over magnesium sulfate. The solvent was evaporated under reduced pressure to yield 4.03 g (96%) of 1-t-butyl-3-hydroxymethyl-3-nitroazetidine (**12**), mp 112-113°C. ^{1}H-NMR (chloroform-*d*): 0.94 (s, 9H)(t-Bu), 3.38 (d, 2H, J = 9 Hz)(C-2,4), 3.61 (bs, 1H)(OH), 3.70 (d, 2H, J = 9 Hz)(C-2,4), 4.19 (s, 2H)(CH_2OH). ^{13}C-NMR (chloroform-*d*): 23.6 (t-Bu), 52.1 (t-Bu), 52.5 (C-2,4), 64.9 (CH_2OH), 81.8 (C-3). ^{15}N- NMR (chloroform-*d*): 11.2 (CNO_2), -342.1 (N-1).

1-t-Butyl-3,3-dinitroazetidines (**6-6d**)

To a solution of the appropriate 1-t-butyl-3-hydroxymethyl-3-nitroazetidine hydrochloride (0.0062 mol) in water (10 ml) was added 40% sodium hydroxide (1.86 g, 0.0186 mol). The mixture was stirred at ambient temperature until a clear solution was obtained (~2.5 h), then the solution was chilled to 10°C. To the chilled solution was added a solution of sodium nitrite (1.71 g, 0.0248 mol) and potassium ferricyanide (0.20 g, 0.00062 mol) in water (5 ml), followed by solid sodium persulfate (1.86 g, 0.0078 mol) in one portion. Cooling was discontinued and the mixture was stirred at ambient temperature for one h. The mixture was extracted with dichloromethane (5 x 5 ml), the extracts were dried (magnesium

sulfate) and the solvent was evaporated under reduced pressure to give the 1-t-butyl-3,3-dinitroazetidine in the yield reported in TABLE 4.

1-t-Butyl-3,3-dinitroazetidinium Nitrates (7-7f)

To a solution of the appropriate 1-t-butyl-3,3-dinitroazetidine (0.002 mol) in dichloromethane (5 ml) was added the appropriate nitric acid (0.002 mol). The resulting mixture was evaporated to dryness and the residue was slurried with dichloromethane and filtered. The collected solid was washed with dichloromethane and dried to yield the 1-t-butyl-3,3-dinitroazetidinium nitrate in the yield reported in TABLE 5.

1,3,3-Trinitroazetidines (8-8g)

To the appropriate 1-t-butyl-3,3-dinitroazetidinium nitrate (0.001 mol) was added acetic anhydride (2 ml) followed by the appropriate ammonium nitrate (0.001 mol). The mixture was heated at 80°C for 3 h, cooled, and treated with water (2.5 ml). The mixture was stirred at 15°C for 16 h, then more water (5 ml) was added and the mixture was cooled to 5°C. The product was collected by filtration, washed with water, and dried to give the 1,3,3-trinitroazetidine in the yield reported in TABLE 6.

1-Methoxycarbonyl-3,3-dinitroazetidines (9-9d)

To a solution of the appropriate 1-t-butyl-3,3-dinitroazetidine (0.002 mol) in dichloromethane (2 ml) was added dibasic sodium phosphate (0.80 g, 0.0056 mol) and methyl chloroformate (2.0 ml, 0.026 mol). The mixture is stirred vigorously at ambient temperature for 8 days. The mixture was filtered, the filter cake was

washed with dichloromethane, and the combined filtrate evaporated to dryness under reduced pressure. The residue was washed with petroleum ether to remove 1-t-butylamino-3-chloro-2,2-dinitropropane and dried to give the 1-methoxycarbonyl-3,3-dinitroazetidine in the yield reported in TABLE 7.

3,3-Dinitroazetidinium Nitrates (11-11d)

The appropriate 1-methoxycarbonyl-3,3-dinitroazetidine (0.0025 mol) is dissolved in methanol (6 ml), then 40% sodium hydroxide (0.536 g, 0.00536 mol) and water (0.3 ml) was added. After 2 h at ambient temperature conversion to the sodium salt of the carbamic acid was complete. To the resulting solution was added concentrated nitric acid (1.0 ml, 0.008 mol). After the gas evolution was complete, the methanol was evaporated and water (10 ml) and 40% sodium hydroxide (0.80 g, 0.008 mole) was added. The solution was extracted with dichloromethane (3 x 5 ml). The extracts were dried over magnesium sulfate and treated with the appropriate nitric acid (0.0025 mol). The resulting mixture was evaporated to dryness and the residue was taken up in dichloromethane. The solid was collected by filtration and dried to give the 3,3-dinitroazetidinium nitrate in the yield reported in TABLE 8.

TABLE 1
3-t-Butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazines

Cpd.	Yield (%)	NMR Chemical Shifts (ppm)[a] ^{1}H	^{13}C	^{15}N
2	90	1.00 (s, 9H)(t-Bu), 2.64 (d, 1H, $J_{H\text{-}H}$ = 12 Hz)(a, C-4), 3.60 (d, 1H, $J_{H\text{-}H}$ = 12 Hz)(e, C-4), 3.65 (d, 1H, $J_{H\text{-}H}$ = 12 Hz)(a, C-6), 3.66 (s, 2H)(CH_2OH), 3.86 (d, 1H, $J_{H\text{-}H}$ = 8 Hz)(a, C-2), 4.47 (d, 1H, $J_{H\text{-}H}$ = 12 Hz)(e, C-6), 4.48 (d, 1H, $J_{H\text{-}H}$ = 8 Hz)(e, C-2), 5.40 (s, 1H)(OH).	26.1 (t-Bu), 48.6 (C-4), 52.2 (t-Bu), 63.9 (CH_2OH), 68.0 (C-6), 80.7 (C-2), 89.2 (C-5).	10.1 (NO_2) -321.2 (N-3)
2a	80	1.00 (s, 9H)(t-Bu).	26.1 (t-Bu), 47.8 (p, $J_{C\text{-}D}$ = 20 Hz) (C-4), 52.2 (t-Bu), 63.1 (p, $J_{C\text{-}D}$ = 22 Hz)(CD_2OD), 67.0 (p, $J_{C\text{-}D}$ = 21 Hz)(C-6), 79.7 (p, $J_{C\text{-}D}$ = 22 Hz)(C-2), 88.7 (C-5).	
2b	84	1.00(s, 9H)(t-Bu), 2.64 (d, 1H, $J_{H\text{-}H}$ = 12 Hz)(a, C-4), 3.60 (dd, 1H, $J_{H\text{-}H}$ = 12 Hz, $J_{C\text{-}H}$ = 3 Hz)(e, C-4), 3.64 (d, 1H, $J_{H\text{-}H}$ = 12 Hz)(a, C-6), 3.65 (s, 2H)(CH_2OH), 3.86 (d, 1H, $J_{H\text{-}H}$ = 8 Hz)(a, C-2), 4.47 (d, 1H, $J_{H\text{-}H}$ = 12 Hz)(e, C-6), 4.48 (d, 1H, $J_{H\text{-}H}$ = 8 Hz)(e, C-2), 5.40 (s, 1H)(OH).	26.1 (t-Bu), 48.6 (d, $J_{C\text{-}C}$ = 39 Hz) (C-4), 52.2 (d, $J_{C\text{-}C}$ = 3 Hz) (t-Bu), 63.9 (d, $J_{C\text{-}C}$ = 38 Hz) (CH_2OH), 67.9 (d, $J_{C\text{-}C}$ = 40 Hz)(C-6), 80.7 (C-2), 89.2 (C-5).	

[a] Spectra determined as methylsulfoxide-d_6 solutions. The natural abundance ^{15}N-NMR spectrum of **2** was obtained on a saturated solution containing chromium(III) acetylacetonate. All ^{1}H and ^{13}C shifts are relative to tetramethylsilane = 0. All ^{15}N shifts are relative to and upfield of external nitromethane = 0.

TABLE 1 (Continued)
3-t-Butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazines

Cpd.	Yield (%)	NMR Chemical Shifts (ppm)[a] ^{1}H	^{13}C	^{15}N
2c	85	1.00 (s, 9H)(t-Bu), 2.62 (dd, 1H, $J_{H\text{-}H}$ = 12 Hz, $J_{N\text{-}H}$ = 5 Hz)(a, C-4), 3.60 (d, 1H, $J_{H\text{-}H}$ = 12 Hz)(e, C-4), 3.65 (d, 1H, $J_{H\text{-}H}$ = 12 Hz)(a, C-6), 3.66 (s, 2H) (CH_2OH), 3.85 (d, 1H, $J_{H\text{-}H}$ = 8 Hz)(a, C-2), 4.47 (d, 1H, $J_{H\text{-}H}$ = 12 Hz)(e, C-6), 4.48 (d, 1H, $J_{H\text{-}H}$ = 8 Hz)(e, C-2), 5.48 (s, 1H)(OH).	26.2 (t-Bu), 48.6 (C-4), 52.2 (t-Bu), 63.9 (CH_2OH), 67.9 (C-6), 80.6 (C-2), 89.1 (d, $J_{C\text{-}N}$ = 6 Hz) (C-5).	10.5 (CNO_2)

[a] Spectra determined as methylsulfoxide-d_6 solutions. All ^{1}H and ^{13}C shifts are relative to tetramethylsilane = 0. All ^{15}N shifts are relative to and upfield of external nitromethane = 0.

TABLE 2
2-t-Butylaminomethyl-2-nitro-1,3-propanediol Hydrochlorides

Cpd.	Yield (%)	NMR Chemical Shifts (ppm)[a] ^{1}H	^{13}C	^{15}N
3	90	1.47 (s, 9H)(t-Bu), 3.87 (s, 2H) (CH_2NH-t-Bu), 4.00 (d, 2H, J_{H-H} = 12 Hz) (CH_2OH), 4.22 (d, 2H, J_{H-H} = 12 Hz) (CH_2OH).	24.5 (t-Bu), 43.7 (CH_2NH-t-Bu), 59.6 (t-Bu), 62.9 (CH_2OH), 92.7 (CNO_2).	6.8 (CNO_2) -321.6 (-$^+$$NH_2$-t-Bu)
3a	57	1.47 (s, 9H)(t-Bu).	24.3 (t-Bu), 42.9 (p, J_{C-D} = 22 Hz) (CD_2ND-t-Bu), 59.3 (t-Bu), 61.9 (p, J_{C-D} = 22 Hz)(CD_2OD), 91.8 (CNO_2).	
3b	85	1.47 (s, 9H)(t-Bu), 3.86 (d, 2H, J_{C-H} = 3 Hz)(CH_2NH-t-Bu), 3.99 (d, 2H, J_{H-H} = 12 Hz)(CH_2OH), 4.22 (dd, 2H, J_{H-H} = 12 Hz, J_{C-H} = 3 Hz)(CH_2OH).	24.6 (t-Bu), 43.8 (d, J_{C-C} = 42 Hz) (CH_2NH-t-Bu), 59.8 (d, J_{C-C} = 4 Hz)(t-Bu), 63.0 (d, J_{C-C} = 37 Hz) (CH_2OH), 92.7 (CNO_2).	
3c	85	1.46 (s, 9H)(t-Bu), 3.86 (d, 2H, J_{N-H} = 3 Hz) (CH_2NH-t-Bu), 3.99 (dd, 2H, J_{H-H} = 12 Hz, J_{N-H} = 4 Hz)(CH_2OH), 4.21 (d, 2H, J_{H-H} = 12 Hz)(CH_2OH).	24.5 (t-Bu), 43.7 (CH_2NH-t-Bu), 59.6 (t-Bu), 62.9 (CH_2OH), 92.6 (d, J_{C-N} = 6 Hz) (CNO_2).	6.7 (CNO_2)

[a] Spectra determined as deuterium oxide solutions. All ^{1}H and ^{13}C shifts are relative to tetramethylsilane = 0. The natural abundance ^{15}N-NMR spectrum of **3** was obtained on a saturated solution containing chromium(III). All ^{15}N shifts are relative to and upfield of external nitromethane = 0.

TABLE 3
1-t-Butyl-3-hydroxymethyl-3-nitroazetidine Hydrochlorides

Cpd.	Yield (%)	NMR Chemical Shifts (ppm)[a] ^{1}H	^{13}C	^{15}N
4	80	@ 25°C: 1.39 (s, 9H)(t-Bu), 4.30 (bs, 2H)(CH_2OH), 4.58 (bs, 2H)(C-2,4), 4.9 (bs, 2H)(C-2,4).	22.4 (t-Bu), 53.2 (C-2,4), 61.0 (t-Bu), 62.6 (CH_2OH), 80.3 (b)(C-3), 83.1(b)(C-3).	1.8, 2.7 (CNO_2) -323.2, -326.2 (N-1)
		@80°C: 1.84 (s, 9H)(t-Bu), 4.76 (s, 2H) (CH_2OH), 5.04 (d, 2H, J_{H-H} = 12 Hz)(C-2,4), 5.29 (d, 2H, J_{H-H} = 12 Hz)(C-2,4).	22.9 (t-Bu), 53.7 (C-2,4), 61.6 (t-Bu), 63.1 (CH_2OH), 82.2 (b)(C-3).	3.0 (CNO_2) -324.3 (N-1)
4a	69	@ 25°C: 1.37 (s, 9H)(t-Bu).	22.1 (t-Bu), 52.6 (p, J_{C-D} = 23 Hz)(C-2,4), 60.8 (t-Bu), 61.4 (p, J_{C-D} = 31 Hz) (CD_2OD), 79-83 (b)(C-3).	
		@ 80°C: 1.84 (s, 9H)(t-Bu).	22.6 (t-Bu), 53.3 (p, J_{C-D} = 23 Hz)(C-2,4), 61.6 (t-Bu), 62.3 (p, J_{C-D} = 24 Hz) (CD_2OD), 82.1 (C-3).	

[a] Spectra determined as deuterium oxide solutions. All ^{1}H and ^{13}C shifts are relative to tetramethylsilane = 0. The natural abundance ^{15}N-NMR spectrum of **4** was obtained on a saturated solution. All ^{15}N shifts are relative to and upfield of external nitromethane = 0.

TABLE 3 (Continued)
1-t-Butyl-3-hydroxymethyl-3-nitroazetidine Hydrochlorides

Cpd.	Yield (%)	NMR Chemical Shifts (ppm)[a] ^{1}H	^{13}C	^{15}N
4b	68	@ 25°C: 1.39 (s, 9H)(t-Bu), 4.30 (bs, 2H)(CH_2OH), 4.58 (bs, 2H)(C-2,4), 4.9 (bs, 2H)(C-2,4).	22.1 (t-Bu), 53.2 (d, $J_{C\text{-}C}$ = 35 Hz)(C-2,4), 60.9 (b)(t-Bu), 62.2 (d, $J_{C\text{-}C}$ = 41 Hz) (CH_2OH), 80.0 (C-3), 82.8 (C-3).	
		@80°C: 1.85 (s, 9H)(t-Bu), 4.75 (d, 2H, $J_{C\text{-}H}$ = 2 Hz)(CH_2OH), 5.04 (d, 2H, $J_{H\text{-}H}$ = 12 Hz)(C-2,4), 5.29 (dd, 2H, $J_{H\text{-}H}$ = 12 Hz, $J_{C\text{-}H}$ = 5 Hz)(C-2,4).	22.6 (t-Bu), 53.8 (d, $J_{C\text{-}C}$ = 34 Hz)(C-2,4), 61.6 (t-Bu), 62.8 (d, $J_{C\text{-}C}$ = 41 Hz)(CH_2OH), 82.1 (C-3).	
4c	72	@ 25°C: 1.39 (s, 9H)(t-Bu), 4.30 (bs, 2H)(CH_2OH), 4.58 (bs, 2H)(C-2,4), 4.9 (bs, 2H)(C-2,4).	22.1 (t-Bu), 53.3 (C-2,4), 60.8 (t-Bu), 62.3 (CH_2OH), 80-83 (b)(C-3).	2.8, 1.6 (CNO_2)
		@80°C: 1.85 (s, 9H)(t-Bu), 4.75 (d, 2H, $J_{N\text{-}H}$ = 3 Hz)(CH_2OH), 5.04 (dd, 2H, $J_{H\text{-}H}$ = 12 Hz, $J_{N\text{-}H}$ = 2 Hz) (C-2,4), 5.29 (d, 2H, $J_{H\text{-}H}$ = 12 Hz)(C-2,4).	22.6 (t-Bu), 53.8 (C-2,4), 61.6 (t-Bu), 62.8 (CH_2OH), 82.2 (bs)(C-3).	3.0 (CNO_2)

[a] Spectra determined as deuterium oxide solutions. All ^{1}H and ^{13}C shifts are relative to tetramethylsilane = 0. All ^{15}N shifts are relative to and upfield of external nitromethane = 0.

TABLE 4
1-t-Butyl-3,3-dinitroazetidines

Cpd.	Yield (%)	NMR Chemical Shifts (ppm)[a] ^{1}H	^{13}C	^{15}N
6	94	0.96 (s, 9H)(t-Bu), 4.03 (s, 4H)(C-2,4).	23.5 (t-Bu), 52.4 (t-Bu), 55.0 (C-2,4), 107.6 (C-3).	-12.1 (CNO_2) -228.8 (N-1)
6a	92	0.95 (s, 9H)(t-Bu).	23.5 (t-Bu), 52.3 (t-Bu), 54.4 (p, $J_{C\text{-}D}$ = 24 Hz) (C-2,4), 107.3 (C-3).	
6b	94	0.96 (s, 9H)(t-Bu), 4.03 (d, 4H, $J_{C\text{-}H}$ = 5 Hz) (C-2,4).	23.5 (t-Bu), 52.4 (d, $J_{C\text{-}C}$ = 5 Hz)(t-Bu), 55.0 (d, $J_{C\text{-}C}$ = 33 Hz (C-2,4), 107.6 (C-3).	
6c	53	0.93 (s, 9H)(t-Bu), 4.00 (t, 4H, $J_{N\text{-}H}$ = 3 Hz) (C-2,4).	23.5 (t-Bu), 52.4 (t-Bu), 54.9 (C-2,4), 107.5 (t, $J_{C\text{-}N}$= 11 Hz)(C-3).	-12.5 (CNO_2)
6d	92	0.96 (s, 9H)(t-Bu), 4.02 (d, 4H, $J_{N\text{-}H}$ = 3 Hz) (C-2,4).	23.5 (t-Bu), 52.4 (t-Bu), 55.0 (C-2,4), 107.5 (d, $J_{C\text{-}N}$= 11 Hz)(C-3).	-12.4 (CNO_2)

[a] Spectra determined as chloroform-*d* solutions. All ^{1}H and ^{13}C shifts are relative to tetramethylsilane = 0. The natural abundance ^{15}N-NMR spectrum of **6** was obtained on a saturated solution containing chromium(III). All ^{15}N shifts are relative to and upfield of external nitromethane = 0.

TABLE 5
1-t-Butyl-3,3-dinitroazetidinium Nitrates

Cpd.	Yield (%)	NMR Chemical Shifts (ppm)[a] ^{1}H	^{13}C	^{15}N
7	95	1.40 (s, 9H)(t-Bu), 5.36 (s, 4H) (C-2,4).	21.8 (t-Bu), 55.0 (C-2,4), 61.8 (t-Bu), 104.4 (C-3).	-4.2 (NO_3^-) -19.9 (CNO_2) -325.5 (N-1)
7a	90	1.40 (s, 9H)(t-Bu).	21.8 (t-Bu), 54.4 (p, $J_{C\text{-}D}$ = 24 Hz)(C-2,4), 61.8 (t-Bu), 104.0 (C-3).	
7b	92	1.40 (s, 9H)(t-Bu), 5.35 (d, 4H, $J_{C\text{-}H}$ = 5 Hz)(C-2,4).	21.8 (t-Bu), 55.0 (d, $J_{C\text{-}C}$ = 37 Hz)(C-2,4), 61.8 (bs)(t-Bu), 104.5 (C-3).	
7c	83	1.40 (s, 9H)(t-Bu), 5.35 (d, 4H, $J_{C\text{-}H}$ = 5 Hz)(C-2,4).	21.8 (t-Bu), 55.0 (d, $J_{C\text{-}C}$ = 36 Hz)(C-2,4), 61.8 (bs)(t-Bu), 104.4 (C-3).	-4.3 (NO_3^-)
7d	61	1.41 (s, 9H)(t-Bu), 5.37 (t, 4H, $J_{N\text{-}H}$ = 2 Hz)(C-2,4).	21.8 (t-Bu), 55.0 (C-2,4), 61.8 (t-Bu), 104.4 (t, $J_{C\text{-}N}$ = 13 Hz)(C-3).	-4.3 (NO_3^-), -20.0 (CNO_2)
7e	86	1.37 (s, 9H)(t-Bu), 5.33 (d, 4H, $J_{N\text{-}H}$ = 2 Hz)(C-2,4).	21.8 (t-Bu), 55.0 (C-2,4), 61.8 (t-Bu), 104.4 (d, $J_{C\text{-}N}$ = 14 Hz)(C-3).	-20.0 (CNO_2)
7f	96	1.37 (s, 9H)(t-Bu), 5.33 (d, 4H, $J_{N\text{-}H}$ = 2 Hz)(C-2,4).	21.8 (t-Bu), 55.0 (C-2,4), 61.8 (t-Bu), 104.4 (d, $J_{C\text{-}N}$ = 14 Hz)(C-3).	-4.3 (NO_3^-), -20.0 (CNO_2)

[a] Spectra determined as deuterium oxide solutions. All ^{1}H and ^{13}C shifts are relative to tetramethylsilane = 0. The natural abundance ^{15}N-NMR spectrum of **7** was obtained on a saturated solution containing chromium(III). All ^{15}N shifts are relative to and upfield of external nitromethane = 0.

TABLE 6
1,3,3-Trinitroazetidines

Cpd.	Yield (%)	NMR Chemical Shifts (ppm)[a] ^{1}H	^{13}C	^{15}N
8	70	5.45 (s)(C-2,4)	64.7 (C-2,4), 105.0 (C-3)	-16.4 (CNO_2), -20.4 (NNO_2), -228.9 (N-1)
8a	75		64.2 (p, $J_{C\text{-}D}$ = 25 Hz)(C-2,4), 104.8 (C-3)	
8b	66	5.45 (d, $J_{C\text{-}H}$ = 5 Hz)(C-2,4)	64.6 (d, $J_{C\text{-}C}$ = 35 Hz)(C-2,4), 104.9 (C-3)	
8c	70	5.45 (dd, $J_{C\text{-}H}$ = 5 Hz, $J_{N\text{-}H}$ = 2 Hz)	64.7 (d, $J_{C\text{-}C}$ = 35 Hz)(C-2,4), 105.0 (C-3)	-20.2 (d, $J_{C\text{-}N}$ = 4 Hz) (NNO_2)
8d	55	5.46 (q, $J_{N\text{-}H}$ = 2 Hz)(C-2,4)	64.7 (C-2,4), 105.0 (t, $J_{C\text{-}N}$ = 11 Hz) (C-3)	-16.2 (CNO_2), -20.2 (NNO_2)
8e	67	5.45 (d, $J_{N\text{-}H}$ = 2 Hz)(C-2,4)	64.7 (C-2,4), 105.0 (d, $J_{C\text{-}N}$ = 11 Hz) (C-3)	-16.2 (CNO_2)
8f	65	5.46 (t, $J_{N\text{-}H}$ = 2 Hz)(C-2,4)	64.7 (C-2,4), 105.0 (d, $J_{C\text{-}N}$ = 11 Hz) (C-3)	-16.2 (CNO_2), -20.2 (NNO_2)
8g	57	5.46 (d, $J_{N\text{-}H}$ = 2 Hz)(C-2,4)	64.7 (C-2,4), 105.0 (C-3)	-20.2 (NNO_2)

[a] Spectra determined as acetone-d_6 solutions. All ^{1}H and ^{13}C shifts are relative to tetramethylsilane = 0. The natural abundance ^{15}N-NMR spectrum of **8** was obtained on a saturated solution containing chromium(III). All ^{15}N shifts are relative to and upfield of external nitromethane = 0.

TABLE 7
1-Methoxycarbonyl-3,3-dinitroazetidines

Cpd.	Yield (%)	NMR Chemical Shifts (ppm)[a] ^{1}H	^{13}C	^{15}N
9	88	3.69 (s, 3H), 4.75 (s, 4H).	53.2 (CH_3), 58.0 (C-2,4), 106.1 (C-3), 156.1 (C=O).	-15.8 (CNO_2) -324.1 (N-1)
9a	49	3.68 (s, 3H).	53.2 (CH_3), 57.5 (p, J_{C-D} = 24 Hz)(C-2,4), 105.9 (C-3), 156.2 (C=O).	
9b	65	3.69 (s, 3H), 4.75 (d, 4H, J_{C-H} = 5 Hz).	53.2 (CH_3), 58.0 (d, J_{C-C} = 33 Hz)(C-2,4), 106.2 (C-3), 156.2 (d, J_{C-C} = 7 Hz)(C=O).	
9c	78	3.68 (s, 3H), 4.74 (t, 4H, J_{N-H} = 2 Hz).	53.2 (CH_3), 58.0 (C-2,4), 106.1 (t, J_{C-N} = 12 Hz)(C-3), 156.1 (C=O).	-16.1 (CNO_2)
9d	85	3.68 (s, 3H), 4.75 (d, 4H, J_{N-H} = 2 Hz).	53.1 (CH_3), 57.9 (C-2,4), 106.3 (d, J_{C-N} = 12 Hz)(C-3), 156.6 (C=O).	-16.1 (CNO_2)

[a] Spectra determined as chloroform-*d* solutions. All ^{1}H and ^{13}C shifts are relative to tetramethylsilane = 0. The natural abundance ^{15}N-NMR spectrum of **9** was obtained on a saturated solution containing chromium(III). All ^{15}N shifts are relative to and upfield of external nitromethane = 0.

TABLE 8
3,3-Dinitroazetidinium Nitrates

Cpd.	Yield (%)	NMR Chemical Shifts (ppm)[a] ^{1}H	^{13}C	^{15}N
11	85	5.24 (s)(C-2,4).	53.8 (C-2,4), 106.8 (C-3)	-4.5 (NO_3^-) -18.2 (CNO_2) -358.6 (N-1)
11a	84		53.3 (p, $J_{C\text{-}D}$ = 25 Hz)(C-2,4), 106.2 (C-3)	
11b	42	5.25 (d, $J_{C\text{-}H}$ = 5 Hz)(C-2,4).	53.8 (d, $J_{C\text{-}C}$ = 35 Hz)(C-2,4), 106.5 (C-3)	-4.3 (NO_3^-)
11c	72	5.24 (t, $J_{N\text{-}H}$ = 2 Hz)(C-2,4).	53.8 (C-2,4), 106.5 (t, $J_{C\text{-}N}$ = 12 Hz)(C-3)	-4.3 (NO_3^-) -18.0 (CNO_2)
11d	86	5.24 (d, $J_{N\text{-}H}$ = 2 Hz)(C-2,4).	53.8 (C-2,4), 106.8 (d, $J_{C\text{-}N}$ = 12 Hz)(C-3)	-18.0 (CNO_2)

[a] Spectra determined as deuterium oxide solutions. All ^{1}H and ^{13}C shifts are relative to tetramethylsilane = 0. The natural abundance ^{15}N-NMR spectrum of **11** was obtained on a saturated solution containing chromium(III). All ^{15}N shifts are relative to and upfield of external nitromethane = 0.

TABLE 9
Unheated Fragmentation of 1,3,3-Trinitroazetidines Using Electron Impact Ionization

Precursor Ion	**8**	**8a**	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**
MW(P)	192	196	193	194	195	193	194	193
$(P\text{-}NO_2)^+$	146S	150S	147S	148S	148S	147S	148S	147S
$(P\text{-}HNO_2)^+$	145S	148S	146S	147S	147S	146M 145S	147M 146S	146S
$(P\text{-}NO_2\text{-}NO)^+$	116T	120T	117T	117T	117T	117T 116T	117T 116T	116T
$(P\text{-}2NO_2)^+$	100T	104T	101T	101T	101T	101T	101T	100T
$(P\text{-}HNO_2\text{-}NO_2)^+$	99S	102S	100S	100S	100S	100S 99S	100S 99S	99S
$(P\text{-}2HNO_2\text{-}NO)^+$	68T	70T	69T	69T	68T	68T	68T	68T
Azetidine Ring	56T 54T 53T 52T	58T 56T 54T	57T 55T 54T 53T	57T 55T 54T 53T	56T 54T 53T 52T	56T 54T 53S 52M	56T 54T 53S 52M	56T 54T 53T 52T
NO_2^+	46B	46B	46B	47B 46T	47B	46B 47T	47B 46S	47B 46S

TABLE 10
Unheated Fragmentation of 1,3,3-Trinitroazetidines Using Chemical Ionization

Precursor Ion	8	8a	8b	8c	8d	8e	8f	8g
MW(P)	192	196	193	194	195	193	194	193
$(P+1)^+$	193B	197B	194B	195B 194M	196B	194B	195B	194B 193M
$(P-NO_2+C_3H_5)^+$	187S	191S	188S	188S	189S	188T	188T	187S
$(P+2-NO_2)^+$	148M	152M	149M	150M	150M	149M	149S	149M
$(P+1-NO_2)^+$	147M	151M	148M	149T	149M	148M	148M	148T
$(P-NO_2)^+$	146S	150S	147S	148L	148S	147T	147S	147M
$(P-NO_2-NO)^+$	116S	120S	117S	118S	118S	117M	118S	117S
$(P+1-2NO_2)^+$	101M	105M	102M	102L	102M	101M	101M	101L
$(P-2NO_2)^+$	100M	103M	101L	101L	101M	100S	100S	100L
$(P-2NO_2-NO)^+$	70T	73T	70T	70T	70T	70T	70T	70T
$(P-3NO_2)^+$	55T	58T	56T	56S	55T	55S	55S	55T
NO_2^+	46S	46S	46S	47S	47S	46S	47M	47S

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