(t, 2 H), 3.53 (t, 3 H); MS, found for $C_{18}H_{14}O$ m/z 246.1046 (calcd m/z 246.1045).

4-Pyrenylacetic Acid (6). Methyl sulfide (0.6 mL, 8.2 mmol) was added to a stirred solution of *N*-chlorosuccinimide (800 mg, 6.0 mmol) in toluene (20 mL) at 0 °C. The resulting mixture was stirred for 5 min at 0 °C and then cooled down to −25 °C. A solution of the alcohol **4** (980 mg, 4.0 mmol) in methylene chloride (4 mL) was added dropwise. The reaction mixture was stirred 2 h at −25 °C, and then a solution of triethylamine (606 mg, 6.0 mmol) in toluene (1 mL) was added dropwise. The cooling bath was removed, and after 5 min ether (40 mL) was added. The organic layer was washed with 1% HCl (10 mL) and water (2 × 30 mL), dried ($MgSO_4$), and concentrated to give 970 mg of crude aldehyde **5** (95% yield according to GC–MS), which was used directly for the next step: IR ($CHCl_3$) 1720 cm^{-1}; NMR ($CDCl_3$) δ 9.92 (t, 1 H), 8.28–7.9 (m, 9 H), 4.22 (d, 2 H); MS, found for $C_{18}H_{12}O$ m/z 244.0888 (calcd m/z 244.0888).

The crude aldehyde from the last step (970 mg) was dissolved in ethanol (30 mL) and added to a solution of silver nitrate (1.4 g, 8.25 mmol) in ethanol (50 mL). To the well-stirred solution of the aldehyde was added dropwise over 10 min 5 N aqueous NaOH (3 mL) diluted to 25 mL with ethanol. The black mixture was stirred at room temperature for 4 h and then centrifuged. The supernatant was decanted, and the solvent was removed under reduced pressure. The residual solid was taken up in water (25 mL) and washed with pentane (2 × 15 mL), acidified with concentrated HCl, filtered, and dried to give 840 mg of acid **6** (81%), mp 241–243 °C (for a small amount that was recrystallized from chlorobenzene): IR (Nujol) 3300–2400, 1700 cm^{-1}; NMR (acetone-d_6) δ 8.4–7.95 (m, 9 H), 4.3 (s, 2 H); MS of the methyl ester of **6** m/z (rel intensity) 274 (38, M^+), 215 (100).

3,4-Dihydrocyclopenta[*cd*]pyrene 3,4-Oxide (2). A solution of the diol **10** (26 mg, 0.1 mmol) and tosyl chloride (1.05 equiv, 20 mg, 0.105 mmol) in monoglyme (0.8 mL) was added slowly to a suspension of sodium hydroxide (10 equiv, 40 mg, 1 mmol) in monoglyme (0.8 mL) at room temperature. The reaction mixture was stirred for 1.5 h at room temperature and filtered, and the filtrate was concentrated. The crude product was chromatographed over a neutral alumina (activity IV) column with benzene under nitrogen stream. The solvent was removed by nitrogen stream to give 20.8 mg of epoxide **2** (86%): mp 204–206 °C; NMR (acetone-d_6) δ 8.32–8.02 (m, 8 H), 5.18 (s, 2 H); MS m/z (rel intensity) 242 (100, M^+), 214 (88), 213 (77).

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Registry No. **2**, 73473-54-8; **3**, 1732-26-9; **4**, 125996-95-4; **5**, 125996-96-5; **6**, 22245-55-2; **10**, 72273-60-0.

Synthesis and X-ray Crystal Structure of 1,3,3-Trinitroazetidine

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1,3,3-Trinitroazetidine (1) was synthesized and its structure elucidated by X-ray crystallography. Reaction of 1-*tert*-butyl-3-((methylsulfonyl)oxy)azetidine (**3a**) with sodium nitrite gave 1-*tert*-butyl-3-nitroazetidine (**4a**), which was converted to 1-*tert*-butyl-3,3-dinitroazetidine (**5a**) by oxidative nitration. Nitrolysis of **5a** with acetyl nitrate gave **1**. 1-Benzhydryl-3,3-dinitroazetidine (**5b**) did not undergo a similar nitrolysis. Single-crystal X-ray analysis of **1** showed that the ring is puckered, with a dihedral angle of 13.6 (5)° between the C–C–C and C–N–C planes, and that the nitramino group exhibits an unusually high (39.4°) out-of-plane deformation. A structural optimization with MNDO reproduced the ring pucker and the nitramino bend to within 5°. The large bend at the ring nitrogen atom indicates sp^3 rather than sp^2 for its hybridization. However, the N–N bond length, 1.351 (6) Å, falls in the normal range for planar (sp^2) nitramines and is ca. 0.1 Å shorter than N–N bonds previously observed in bent nitramines.

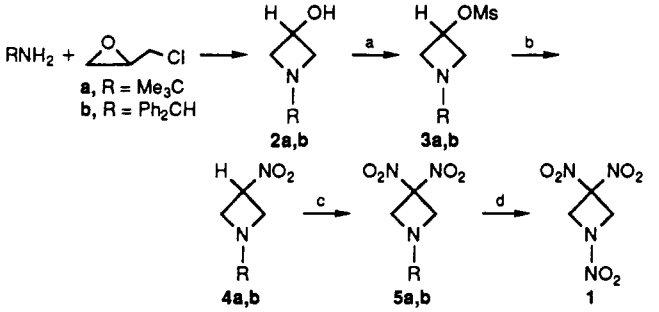
Introduction

Cyclic polynitramines[1] as well as cyclic nitramines containing *gem*-dinitro groups[2] are of interest for structural and decomposition mechanism studies.[3] 1,3,3-Trinitroazetidine (**1**), the simplest member of the latter class, has been synthesized in these laboratories, and thermolysis[4] infrared dynamic motion studies[5] of this material have been reported elsewhere. Herein we report the synthesis and crystallographic characterization of **1**.

Synthesis

The Mannich condensation reaction between amines and nitro alcohols[6] has been employed to synthesize cyclic compounds containing both *C*-nitro and nitramino groups.[2,7] This approach depends on the use of a sterically demanding blocking group on the amine to control the course of the ring formation.[2b] Subsequent nitrolysis of the N-blocking group yields the nitramine. Both acyl and alkyl groups have been used, although results are highly dependent on the system.[8] However, the Mannich condensations used in the synthesis of relatively unstrained

Scheme I[a]



[a] Reagents: (a) Et_3N, $MeSO_2Cl$; (b) $NaNO_2$; (c) $AgNO_3$, $NaNO_2$ or $C(NO_2)_4$; (d) HNO_3, $(CH_3CO)_2O$.

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[‡] Naval Research Laboratory.

(1) (a) Koppes, W. M.; Chaykovsky, M.; Adolph, H. G.; Gilardi, R.; George, C. *J. Org. Chem.* **1987**, *52*, 1113. (b) Willer, R. L.; Atkins, R. L. *J. Org. Chem.* **1984**, *49*, 5147. (c) Willer, R. L. *J. Org. Chem.* **1984**, *49*, 5151.

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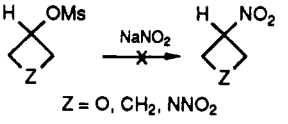
6- to 8-membered rings[2] did not give azetidines.[9]

An alternative approach (Scheme I) is the stepwise introduction of C-NO_2 groups to azetidines that contain functional groups at the 3-position. In the present study, 1-alkyl-3-azetidols,[10] where the alkyl group was *tert*-butyl (**2a**) or benzhydryl (**2b**), were prepared from epichlorohydrin and the corresponding amines. These alcohols were then reacted with methanesulfonyl chloride to give the corresponding mesylates, **3a** and **3b**.[11]

Displacement of the mesylate groups from **3a** and **3b** by sodium nitrite was found to give the corresponding 3-nitro compounds, **4a** and **4b**, under limited conditions. The *tert*-butyl derivative **3a** did not give **4a** in solvents such as DMF or DMSO, which are usually used for nitrite ion displacement reactions. Compound **4a** was obtained in 8% yield after 16 h at 0 °C using aqueous methanol containing phloroglucinol. Nitro compound **4a** was unstable in solution, and higher reaction temperatures resulted in decomposition. No **4a** was obtained when the bromo[12] derivative or *p*-tosylate[13] was used in place of the mesylate. The *N*-benzhydryl mesylate **3b** had low solubility in aqueous methanol and did not react with nitrite ion under conditions used with the *tert*-butyl derivative. The 3-nitro compound **4b** was obtained in 11% yield in the presence of sodium iodide using DMF solvent; heating for several days at 50 °C was required. No reaction took place in the absence of iodide ion, indicating that the 3-iodo derivative (**6**) was an intermediate.

The nitrite ion displacement reaction of **3a** or **3b** may be compared to similar reactions in other four-membered-ring compounds. With the exception of the reaction of 3-halocyclobutenes with nitrite ion to give the corresponding 3-nitrocyclobutenes[14] by S_N2' displacement, the synthesis of nitro derivatives of four-membered-ring compounds by nucleophilic displacements has not been described previously.[15] 3-Nitrooxetane[16] and 1-nitrocyclobutane[15] were prepared by oxidation of the corresponding amines or oximes after attempted nitrite ion displacements of halides or tosylates were unsuccessful. Displacement on the oxetane rings by other nucleophiles[17] such as azide or halide ions required temperatures over 100 °C.



Oxidative nitration of the salts of **4a** and **4b** gave the corresponding 3,3-dinitroazetidines **5a** and **5b**. The *tert*-butyl compound **5a** was prepared in 39% yield by reaction with aqueous sodium nitrite and silver nitrate[18a] or in 60% yield by the potassium ferricyanide–sodium persulfate procedure.[18b] The salt of the mononitro benzhydryl derivative **4b**, which was not water soluble, gave a 38% yield of **5b** with sodium nitrite and tetranitromethane using ethanol as a cosolvent. Compounds containing *gem*-dinitro groups β to amine functionality are expected to be unstable,[19] and although **5a** was stable at room temperature, attempted distillation of this compound above 120 °C resulted in explosive decomposition.

The *tert*-butyl group of **5a** failed to undergo nitrolysis with hot mixed nitric and sulfuric acids but did react with acetyl nitrate in acetic acid at 0 °C to give a 35% yield of 1,3,3-trinitroazetidine (**1**). Reaction of alcohol **2a** or mesylate **3a** with acetyl nitrate solutions under similar conditions gave 1-*tert*-butyl-3-nitratoazetidine or the nitric acid salt of **3a**, respectively, but no nitramine product. The presence of strongly electron withdrawing groups,[2b] such

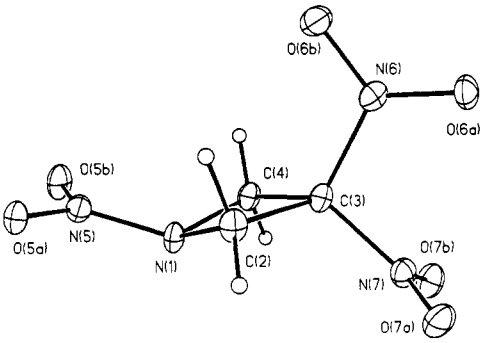


Figure 1. Thermal ellipsoid plot with non H atoms of 1,3,3-trinitroazetidine drawn at the 20% probability level.

Table I. Bond Lengths (Å) and Bond Angles (deg)

N(1)–C(2)	1.485 (7)	N(1)–C(4)	1.474 (6)
N(1)–N(5)	1.351 (6)	C(2)–C(3)	1.534 (7)
C(3)–C(4)	1.545 (7)	C(3)–N(6)	1.517 (7)
C(3)–N(7)	1.493 (7)	N(5)–O(5a)	1.218 (5)
N(5)–O(5b)	1.236 (5)	N(6)–O(6a)	1.214 (5)
N(6)–O(6b	1.223 (6)	N(7)–O(7a)	1.217 (6)
N(7)–O(7b)	1.212 (6)		
C(2)–N(1)–C(4)	95.1 (4)	C(2)–N(1)–N(5)	120.4 (4)
C(4)–N(1)–N(5)	122.4 (4)	N(1)–C(2)–C(3)	86.6 (4)
C(2)–C(3)–C(4)	90.3 (4)	C(2)–C(3)–N(6)	114.5 (4)
C(4)–C(3)–N(6)	114.2 (4)	C(2)–C(3)–N(7)	116.2 (4)
C(4)–C(3)–N(7)	116.2 (4)	N(6)–C(3)–N(7)	105.6 (4)
N(1)–C(4)–C(3)	86.5 (3)	N(1)–N(5)–O(5a)	118.4 (4)
N(1)–N(5)–O(5b)	116.3 (4)	O(5a)–N(5)–O(5b)	125.3 (4)
C(3)–N(6)–O(6a)	118.8 (4)	C(3)–N(6)–O(6b)	115.2 (4)
O(6a)–N(6)–O(6b)	125.9 (5)	C(3)–N(7)–O(7a)	116.3 (4)
C(3)–N(7)–O(7b)	117.1 (4)	O(7a)–N(7)–O(7b)	126.5 (5)

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as the ring *gem*-dinitro groups in **5a**, may be required for removal of the alkyl blocking group on nitrogen by nitrolysis.

The dinitro compounds **5a** and **5b** formed stable salts with anhydrous hydrogen bromide, nitric acid, or triflic acid. Bromine reacted with **5a** to give a stable 1:1 adduct, from which **5a** could be regenerated without decomposition. Attempts to convert compound **5b** to **1** by nitrolysis gave complex aromatic nitration products, but no N-NO_2 compounds. Reductive dephenylation of **5b** with hydrogen on palladium resulted in loss of ring nitro groups.

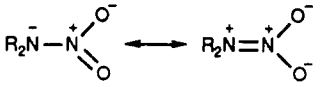
X-ray Crystal Structure Analysis

Although several crystallographic analyses of substituted azetidines are available, structural studies of nitramines in four-membered rings[20] have not been reported. The geometry of **1** is illustrated in Figure 1, and bond distances and angles are given in Table I. The ring is significantly puckered, with an angle between the C–C–C and C–N–C planes, ϕ, of 13.6 (5)°. An electron-diffraction study[21] reported ϕ = 33.1° for unsubstituted azetidine in the gas phase. X-ray structural studies of a number of azetid*inium* compounds[22] indicate typical values of 10–14° for ϕ, though examples exist from ϕ = 0, for 1,1-dibenzyl-3,3-dimethylazetidinium bromide,[22d] to ϕ = 26° for 1-(1-methyl-2-phenylethyl)-2-methyl-3-hydroxyazetidinium chloride.[22e]

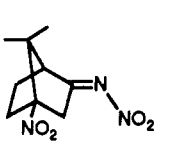
The two nitro groups bonded to C(3) are essentially perpendicular to one another; the pertinent torsion angles N(7)–C(3)–N(6)–O(6A) and N(6)–C(3)–N(7)–O(7A) are –0.4 (6) and 89.2 (6)°, respectively.

The amino nitrogen, N(1), is pyramidal; one measure of this is the "out-of-plane bend" angle between the N–N bond and the C–N–C plane, which is 39.4°. The same bend angle would be 54.5° for a pseudotetrahedral sp^3 amine and 0° for a planar sp^2 amine, so **1** is geometrically closer to sp^3 hybridization. This bend is much larger than that normally observed in nitramines. A survey of the geometries of 30 nitramine groups reported in the crystal structure determinations (Table II) indicates an average value of 12.2°, a most probable value of 0° (which differs from the average because the distribution is skewed), and a wide range, 0–59°, for this bend. Only one compound (**8**) is more sharply bent than **1**.

The N–N bond length in **1** is 1.351 Å. This is consistent with N–N bond lengths observed (1.35–1.40 Å, see Table II) for nitramines in 5- and 6-membered rings but is unexpectedly short for a compound with a large twist or bend between the C–N–C plane and the NO_2 plane. The shortened N–N bond lengths and planar amino geometry usually seen together in nitramines have been explained[23] by invoking conjugation of a "p"-type lone pair on the amino nitrogen with the π-electron system of the nitro group.



In molecules where steric repulsions prohibit coplanarity, such as 4,N-dinitrobornan-2-imine (**7**),[24] and N-nitroaziridine (**8**),[25] no bond shortening is observed. In **7**, the nitro group is *twisted* ca. 90° from the imino (CNN) plane, and the N–N distance is 1.461 Å; in **8**, the CNC plane is *bent* 59° from the nitro plane, and the N–N bond length is 1.439 Å.



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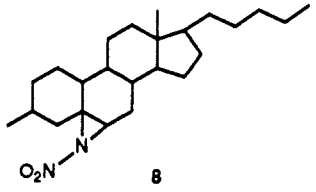

8

In addition to the large out-of-plane angle, the ring strain of the four-membered ring in **1** may cause the ring nitrogen to use a hybrid orbital with considerable s character for its lone pair, further decreasing the effectiveness of lone pair-π overlap.[26] This is suggested by the ultraviolet

Table II.[27] Nitramine Bond Distances and Bend Angles

	out-of-plane angle, deg	N–N distance, Å
cyclic		
DINGU[28]	0.0	1.360
DINGU[28]	13.0	1.386
β-HMX[29]	21.1	1.373
β-HMX[29]	8.0	1.354
α-HMX[30]	12.2	1.367
α-HMX[30]	3.3	1.354
δ-HMX[31]	0.0	1.346
δ-HMX[31]	0.0	1.355
δ-HMX[31]	9.9	1.392
δ-HMX[31]	22.5	1.363
RDX[32]	19.9	1.351
RDX[32]	33.3	1.392
RDX[32]	33.9	1.398
DADN[33]	20.3	1.352
DPT[34]	25.5	1.347
DPT[34]	34.9	1.386
1	39.4	1.351
8[25]	59.0	1.439
acylic		
TETRYL[35]	11.2	1.348
BTNENO[36]	8.7	1.392
BTNENO[36]	3.3	1.375
BSX[37]	0.0	1.387
BSX[37]	19.9	1.358
BSX·DMF[38]	0.0	1.370
BSX·DMF[38]	8.6	1.355
BXS·DMF[38]	0.0	1.370
BSX·DIOX[39]	0.0	1.379
BSX·DIOX[39]	6.6	1.387
BSX·DIOX[39]	0.0	1.355
DNEDN[40]	0.0	1.357
$(CH_3)_2NNO_2$[41]	0.0	1.335

(20) (a) Only one example of a N-NO_2 azetidine has been reported (without structure determination): Bumgardner, C. L.; McCallum, K. S.; Freeman, J. P. *J. Am. Chem. Soc.* **1961**, *83*, 4417. (b) Zacharis, H. M.; Trefonas, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 2935.

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(27) The numbers of nitramines quoted refer to the number of crystallographically independent groups for which structural parameters were derived; this may be more or less than the number per molecule.

(28) DINGU: 2,6-dinitro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione, Boileau, J.; Wilmer, E.; Gilardi, R.; Stinecipher, M.; Gallo, R.; Pierrot, M. *Acta Crystallogr.* **1988**, *C44*, 696.

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spectrum of 1, which shows a maximum at 240 nm, ϵ 3600, compared with 1-nitroazetidine at 240 nm, ϵ 4400, and nitrodipropylamine at 244 nm, ϵ 6500.[20a] The shift observed for 1 may be associated with the strain imposed by increased N–N double bond character in the polar excited state of the small ring derivatives.

In summary, the pronounced nonplanarity of the nitramine indicates that the shortened N–N bond distance in 1 is probably not the result of increased double bond character. The explanation may lie rather in an analysis of the inductive effects produced by the strongly electron withdrawing geminal dinitro grouping across the ring. A conformational estimate free from solid-state effects was obtained from MNDO (semiempirical quantum chemical) calculations. Values of 9.2° and 37° were obtained for the ring dihedral and the amino bend angles, in good agreement with the observed values (13.6 and 39.4°). The independent arrival at similar conformational parameters strongly indicates that they are intrinsic features of the molecule and not distortions caused by crystal packing forces.

Experimental Section[42]

Caution. Nitro azetidines may be sensitive to heat or shock and must be handled with caution behind appropriate shielding.

1-*tert*-Butyl-3-nitroazetidine (4a). A solution of mesylate **3a**[11] (40 g, 0.25 mol), phloroglucinol dihydrate (32 g, 0.20 mol), and sodium nitrite (25 g, 0.36 mol) in methanol (300 mL) and water (30 mL) was stirred at 0 °C for 16 h. The solution was concentrated to one-third its original volume at 30 °C in vacuo, water (200 mL) was added, and the unstable mixture was extracted rapidly with CH_2Cl_2 (3 × 100 mL). The combined extracts were dried ($MgSO_4$), the solvent was evaporated, and the residue was distilled to give 2.5 g (8%) of **4a**, bp 50–53 °C (0.1 mmHg): IR 3000, 1550, 1430 cm^{-1}; NMR δ 0.95 (s, 9 H), 3.55 (asym d, J = 3 Hz, 4 H), 4.90 (quint, J = 3 Hz, 1 H). Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.72. Found: C, 52.87; H, 8.66.

1-Benzhydryl-3-nitroazetidine (4b). A solution of mesylate **3b**[11] (31.5 g, 0.10 mol), sodium nitrite (7.5 g, 0.11 mol), sodium iodide (14.0 g, 0.10 mol), and phloroglucinol dihydrate (12 g, 0.075 mol) in water (20 mL) and DMF (200 mL) was stirred at 50 °C for 48 h. The solution was cooled, diluted with water (200 mL), and extracted with ether (3 × 100 mL). The combined extracts were washed with water and dried ($MgSO_4$), and the solvent was evaporated to give 14.1 g of an oil which after column chromatography on silica gel (CH_2Cl_2) gave 3.0 g (11%) of **4b**, mp 135–136 °C: IR 1550, 1440 cm^{-1}; NMR δ 3.5 (asym d, J = 3 Hz, 4 H), 4.3 (s, 1 H), 4.8 (m, 1 H), 7.0 (m, 10 H). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.21; H, 6.50; N, 10.10. Further elution gave 4.5 g (13%) of 1-benzhydryl-3-iodoazetidine (6), mp 96–97 °C: NMR δ 3.6 (m, 4 H), 4.2 (m, 1 H), 4.4 (s, 1 H), 7.0 (m, 10 H). Anal. Calcd for $C_{16}H_{16}NI$: C, 55.02; H, 4.62; N, 4.00. Found: C, 55.29; H, 4.80; N, 4.03.

1-*tert*-Butyl-3,3-dinitroazetidine (5a). Freshly distilled **4a** (3.2 g, 0.020 mol) was dissolved in a solution of sodium hydroxide (0.84 g, 0.021 mol) in water (50 mL) and cooled to 10 °C. A chilled solution of sodium nitrite (6.9 g, 0.10 mol) and potassium ferricyanide (1.3 g, 0.004 mol) in water (50 mL) was added, followed by solid sodium persulfate (6.6 g, 0.028 mol). The temperature rose rapidly to 30 °C, and the mixture was stirred for 1 h and then extracted with CH_2Cl_2 (2 × 50 mL). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated. The residual liquid was distilled to give 2.44 g (60%) of **5a**, bp 70–72 °C (0.2 mmHg), mp 17–18 °C: IR 3050, 1580, 1465 cm^{-1}; NMR δ 1.0 (s, 9 H), 4.2 (s, 4 H). Anal. Calcd for $C_7H_{13}N_3O_4$: C, 41.38; H, 6.45; N, 20.68. Found: C, 41.66; H, 6.57; N, 20.11.

1-Benzhydryl-3,3-dinitroazetidine (5b). A solution of **4b** (1.0 g, 3.7 mmol) and sodium hydroxide (0.30 g, 7.5 mmol) in ethanol (30 mL) was stirred for 30 min at ambient temperature, and sodium nitrite (1.0 g, 14 mmol) was added. Tetranitromethane (1.0 g, 5.0 mmol) was added dropwise at 30 °C. After 30 min, the solvent was evaporated, water (50 mL) was added, and the mixture was extracted with ether (2 × 50 mL). The combined extracts were dried ($MgSO_4$), and the solvent was evaporated to give a waxy solid, which was recrystallized (ethanol) to give 0.44 g (38%) of **5b**, mp 85–86 °C: IR 1580, 1460 cm^{-1}; NMR δ 3.95 (s, 4 H), 4.4 (s, 1 H), 7.1 (m, 10 H). Anal. Calcd for $C_{16}H_{15}N_3O_4$: C, 61.33; H, 4.80; N, 13.42. Found: C, 61.34; H, 5.06; N, 13.23.

1,3,3-Trinitroazetidine (1). Acetic anhydride (5 mL) was cooled with an ice bath to 2 °C, and 98% nitric acid (1.5 mL) was added, dropwise, at a rate such that the temperature was maintained at 10 °C. The solution was stirred for 5 min, and then **5a** (0.75 g, 3.7 mmol) was added dropwise. After 1 h, CH_2Cl_2 (50 mL) was added, and the solution was washed with water (2 × 50 mL) and with 10% aqueous sodium carbonate (50 mL) and then dried ($MgSO_4$). The solvent was evaporated, and the residual solid was recrystallized (CCl_4) to give 0.25 g (35%) of **1**, mp 103–104 °C: IR 3050, 1580, 1420 cm^{-1}; H NMR δ 5.2 (s): ^{13}C NMR δ 103.4, 63.4; density ($AgNO_3$ solution flotation) 1.83. Mass Spectrum and Anal. Calcd for $C_3H_4N_4O_6$: mol wt, 192.0131; C, 18.76; H, 2.10. Found: 192.0134; C, 18.93; H, 2.16.

Experimental X-ray analysis of 1,3,3-trinitroazetidine (1): $C_3H_4N_4O_6$, M_r = 192.06, orthorhombic space group *Pbca*, a = 5.733 (1) Å, b = 11.127 (2) Å, c = 21.496 (4) Å, V = 1371.3 (3) Å^3, Z = 8, D_x = 1.861 mg m^{-1} (at −30 °C), D_x = 1.84 (at 20 °C), λ(Cu Kα) = 1.541 78 Å, μ = 1.56 mm^{-1}, $F(000)$ = 784, data collection T = −30 °C, Final R = 0.072, R_w = 0.060 for 759 independent reflections with $F_o > 3\sigma(F_o)$.

A clear colorless 0.18 × 0.20 × 0.50 mm crystal recrystallized from carbon tetrachloride was used for data collection on an automated Nicolet R3m/V diffractometer with incident beam monochromator, 25 centered reflections within $20 < 2\theta < 60°$ were used for determining lattice parameters. $(\sin(\theta)/\lambda)_{max}$ = 0.575 Å^{-1}, range of hkl $-6 \le h \le 5$, $-11 \le k \le 12$, and $0 \le l \le 24$. Standard reflections $\bar{2}02$, 040, 008 monitored every 60 reflections with random variations up to ±1.7% over data collection, $\theta/2\theta$ mode, scan width $[2\theta(K_{\alpha 1}) - 1.0]$ to $[2\theta(K_{\alpha 2}) + 1.0]°$, 2θ scan rate ranged from 2° min^{-1} to 30° min^{-1} dependent on count rate; 2514 reflections were measured, 1071 unique, 759 observed with $F_o > 3\sigma(F_o)$; R_{int} = 0.014 from merging duplicate reflections. Data were corrected for Lorentz and polarization, and an empirical absorption correction was applied. The maximum and minimum transmission values were 0.94 and 0.41. Structure was solved by direct methods. The blocked least-squares refinement minimized the quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$, g = 0.0003. Secondary extinction parameter p = 0.0010 (3) in $F_c^* = F_c/[1.0 + 0.002(p)F_o^2/\sin(2\theta)]^{0.25}$. There were 131 parameters refined: all atom coordinates, anisotropic temperature parameters for non-hydrogen atoms; the hydrogen atoms were assigned fixed isotropic thermal parameters. $(\Delta/\sigma)_{max}$ = 0.001, R = 0.072, R_w = 0.060, S = 1.47. Final difference Fourier excursions 0.36 and −0.43 e Å^{-3}. Atomic scattering factors from *International Tables for Crystallography*.[43] The programs used for structure solution,

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refining, and plotting are part of SHELXTL.[44]

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Registry No. 1, 97645-24-4; **3a**, 46236-54-8; **3b**, 33301-41-6; **4a**, 125735-36-6; **4b**, 125735-37-7; **5a**, 125735-38-8; **5b**, 125735-39-9; **6**, 125735-40-2.

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Supplementary Material Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters (1 pages); table of calculated structure factors for 1,3,3-trinitroazetidine (4 pages). Ordering information is given on any current masthead page.

Improved Method for the Wacker Oxidation of Cyclic and Internal Olefins[1]

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An improved method for palladium(II)-catalyzed Wacker oxidation of cyclic and internal olefins is described. Addition of perchloric, sulfuric, nitric, or tetrafluoroboric acid to a chloride free solution of the Pd(II) catalyst gives rate enhancements of up to a factor of 50. The oxidation of cyclohexene to cyclohexanone, which was previously reported to give a 97% yield after 5 h, is now accomplished in 1 h quantitatively, with only one-third of the amount of Pd(II) used. Limitations of the method are also discussed.

The palladium(II) oxidation of terminal olefins to give methyl ketones (Wacker oxidation) is well established both as an industrial and an organic synthetic process (eq 1).[2,3] Chemical oxidants (Ox) such as Cu(II), Fe(III), MnO_2, heteropolyacids, or quinones are used to regenerate Pd(II) from Pd(0) (eq 2),[4-10] thus making the reactions catalytic with respect to the Pd(II). Recently, electrochemical regeneration of Pd(II) in these systems has been reported.[11-13]

$$RCH{=}CH_2 + Pd(II) \xrightarrow{H_2O} RC(O)CH_3 + Pd(0) \quad (1)$$

$$Pd(0) + Ox \rightarrow Pd(II) + Red \quad (2)$$

One of the deficiencies of this reaction is that the oxidation of cyclic and internal olefins is inefficient.[3] On the other hand, it is clear from early industrial work[7,14-16] and the patent literature[17,18] that the homogeneous oxidation of ethylene and terminal olefins is accelerated by addition of small amounts of acid but is inhibited by acid at high concentrations and by chloride.[7,14-16,19] However, the influence of acid on cyclic olefins is less certain. Moiseev et al.[20] indicated that the cyclohexene oxidation rate was independent of $[H^+]$, whereas Kolb et al.[8] and Horowitz[12] demonstrate that the cyclic olefin oxidation rate is en-

Table I. The Effect of Acid of the Wacker Oxidation of 1-Decene

acid (% conv)[a]	products	yield, %
HCl (0)	no reaction	-
H_2SO_4 (93)	2-decanone	64
	3-decanone	5
	4-decanone	14
		(90)[b]
HNO_3 (93)	2-decanone	83
	3-decanone	6
	decanal	4
		(100)[b]
$HClO_4$ (98)	2-decanone	79
	3-decanone	10
	decanal	4
		(95)[b]
HBF_4 (99)	2-decanone	84
	3-decanone	9
	decanal	3
		(97)[b]

[a] Conversion of 1-decene after 10-min reaction at 60 °C using 0.25 M acid. [b] Material balance based on starting material.

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