CH_2=C=CHOMe, 13169-00-1; PhNHOH, 100-65-2; MeNHOH·HCl, 4429-44-1; *t*-BuNHOH·HCl, 57497-39-9; CH_2=C=C-$CH_3CO_2CH_3$, 18913-37-6; CH_3CH=C=$CCH_3CO_2CH_3$, 57585-04-3; CH_2=C=$CHCO_2CH_3$, 18913-35-4; CH_2=C=$CHCO_2CH_2CH_3$, 14369-81-4; $PhSO_2C$≡CCH_3, 2525-41-9; CH_2=C=CCH_3SO_2Ph, 13603-90-2; CH_2=C=CH_2, 463-49-0; CH_2=C=CHCN, 1001-56-5; *C,N*-diphenylnitrone, 1137-96-8; *N*-methyl-*C*-phenylnitrone, 3376-23-6.

Synthesis of Polynitrocyclobutane Derivatives

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The synthesis of polynitrocyclobutanes was studied. Oxidation of oximinocyclobutanes with hypochlorite followed by Zn reduction gave ethyl 3-nitrocyclobutanecarboxylate (**4a**), diethyl 3-nitrocyclobutane-1,1-dicarboxylate (**4b**), and 2,5,8,10-tetranitrodispiro[3.1.3.1]decane (**4d**) in 20–90% yields. Oxidation of aminocyclobutanes with *m*-chloroperbenzoic acid gave 1-nitrocyclobutane (**4e**), 1,3-dinitrocyclobutane (**4f**), and 2,8-dinitrodispiro[3.1.3.1]decane (**4c**) in 20–40% yields. Bromination of **4f** gave 1,3-dibromo-1,3-dinitrocyclobutane (**5**). Addition of N_2O_4 to methyl or ethyl bicyclo[1.1.0]butane-1-carboxylates gave methyl or ethyl 1,3-dinitrocyclobutanecarboxylates (**7a,b**) in 17% and 40% yields. Oxidative nitration of nitrocyclobutanes **4a,d,e** gave the corresponding *gem*-dinitrocyclobutanes in 15–78% yield. 1,1,3,3-Tetranitrocyclobutane (**8f**) and 1,1,3-trinitrocyclobutane (**11**) were obtained by similar oxidative nitration of **4f** or **7a,b** in 20–40% yields. Dispirane **4c** was converted similarly to 5,5,10,10-tetranitrodispiro[3.1.3.1]decane in 64% yield.

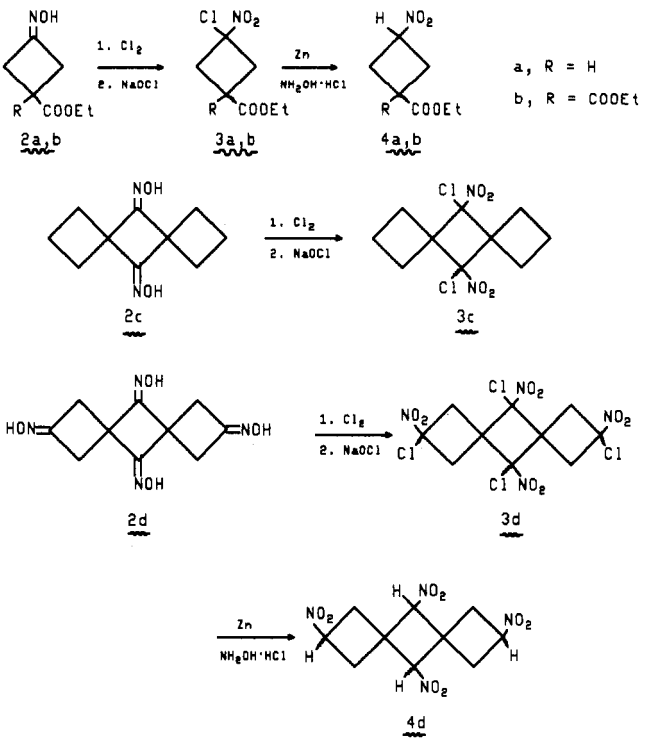
Introduction

Although there has been considerable current interest in the synthesis of cyclic polynitro compounds,[1] nitrocyclobutanes are relatively unstudied. Reported examples of this class of compounds are 1-nitrocyclobutane[2] and several phenyl-substituted derivatives.[3] The preparation of nitrocyclobutanes is complicated by the fact that standard nitrite ion displacements of cyclobutyl halides or tosylates is too slow to be of practical synthetic value.[4] We report here the synthesis of several highly nitrated cyclobutane derivatives, including the first examples of *gem*-dinitrocyclobutanes and nitro derivatives of dispiro-[3.1.3.1]decane.

Results and Discussion

Ethyl 3-oxocyclobutanecarboxylate[5] (**1a**), diethyl 3-oxocyclobutane-1,1-dicarboxylate[6] (**1b**), 5,10-dioxo-

Scheme I



dispiro[3.1.3.1]decane[7] (**1c**), and 2,5,8,10-tetraoxodispiro-[3.1.3.1]decane (**1d**) were prepared and converted to the corresponding oximes in 56–90% yields. The oximes **2a–d** were converted to the *gem*-chloronitro derivatives, **3a–d**, in 89–90% yields (Scheme I), employing chlorine gas and subsequent oxidation of the unisolated *gem*-chloronitroso intermediates with alkaline chlorine bleach under phase-transfer conditions.[8] The reduction of **3a**, **3b**, and **3d** with

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(3) Nitrocyclobutanes have been prepared by photocyclization of β-nitrostyrene with olefins, and 1-phenyl-3,3-difluoro-4,4-dichlorocyclobutane reacts with sodium nitrite to give a nitrocyclobutene derivative by S_N2' displacement reaction. These reactions have been limited to the synthesis of phenyl-substituted cyclobutane rings. (a) Farnum, D. G.; Mostashari, A. *J. Org. Photochem. Synth.* **1976**, *2*, 79. (b) Chapman, O. L.; Griswold, A. A.; Hoganson, E.; Lenz, G.; Reasoner, *J. Pure Appl. Chem.* **1964**, *9*, 585. (c) Scheeren, H. W.; Frissen, A. E. *Synthesis* **1983**, 794. (d) Breslow, R.; Kievelevich, D.; Mitchell, M. J.; Fabian, W.; Wendel, K. *J. Am. Chem. Soc.* **1965**, *87*, 5132. (e) Miller, D. B.; Flanagan, P. W.; Shechter, H. *J. Org. Chem.* **1976**, *41*, 2112.

(4) During this study, no detectable amounts of 1-nitrocyclobutane were observed when sodium nitrite and 1-bromocyclobutane were stirred in DMSO at ambient or 100 °C for 24 h. However, some reactivity of cyclobutyl halides in DMSO with nitrite form of an anion-exchange resin has been reported: Yamada, R.; Noguchi, T.; Urata, Y.; Okabe, K. *Mem. Def. Acad., Math., Phys., Chem. Eng., Yokosuka, Jpn.* **1974**, *14*, 123; *Chem. Abstr.* **1977**, *86*, 29155r.

(5) Cripps, H. N.; Williams, J. K.; Sharkey, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 2723.

(6) Avram, M. A.; Nenitzescu, C. D.; Maxim, M. *Chem. Ber.* **1957**, *90*, 1424.

(7) Erickson, J. L. E.; Collins, F. E.; Owens, B. L. *J. Org. Chem.* **1966**, *31*, 480.

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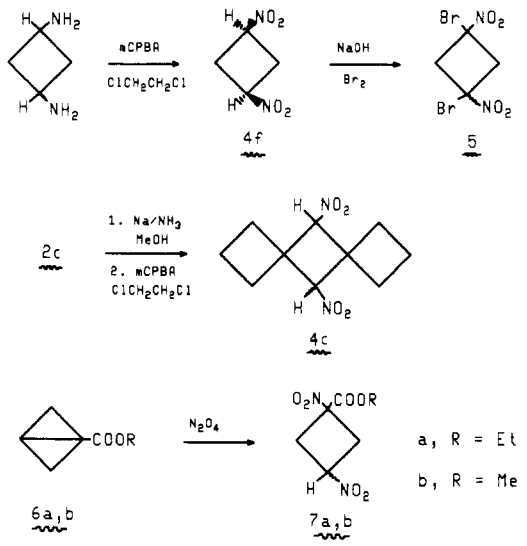
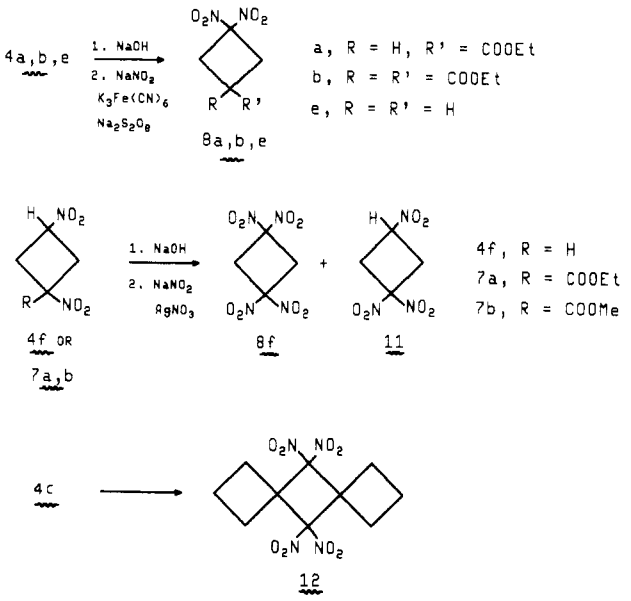
Scheme II



Scheme III



zinc and hydroxylamine hydrochloride[8] gave ethyl 3-nitrocyclobutanecarboxylate (**4a**, isomers), diethyl 3-nitrocyclobutane-1,1-dicarboxylate (**4b**), and 2,5,8,10-tetranitrodispiro[3.1.3.1]decane (**4d**, mixture of isomers) in 80%, 78%, and 20% yields, respectively. The disubstituted derivative **3c**, which was quite insoluble, was not reduced under these conditions or by hydrogenation over palladium on carbon.

Oxidation of aminocyclobutanes with *m*-chloroperbenzoic acid in refluxing dichloroethane was found to give moderate yields of the corresponding nitro derivatives. Thus, 1-aminocyclobutane gave 1-nitrocyclobutane[9] (**4e**) in 34% yield. Similarly, oxidation of 1,3-diaminocyclobutane[6] gave a 38% yield of a mixture of *cis*- and *trans*-1,3-dinitrocyclobutanes (**4f**) (Scheme II), which, during purification by chromatography on silica gel, epimerized to the cis isomer. The dinitro dispirane **4c** was obtained in 15% yield by the reduction of dioxime **2c** to the corresponding diamine with sodium in liquid ammonia followed by oxidation of the diamine with *m*-chloroperbenzoic acid.

An alternate route to nitrocyclobutanes based on the addition of N_2O_4 to bicyclo[1.1.0]butane was investigated, but this reaction failed to give dinitro compound **4f** over a range of temperatures from −78 °C to ambient. However, a report[10] describing the addition of N_2O_4 to methyl 1-tricyclo[4.1.0.0^{2,7}]heptanecarboxylate prompted us to investigate the addition to bicyclo[1.1.0]butane-1-carboxylate esters. Reaction of the ethyl ester,[11] **6a**, with N_2O_4 gave ethyl 1,3-dinitrocyclobutane-1-carboxylate as a mixture of cis/trans isomers (**7a**) in 40% yield. The methyl ester **7b** was similarly obtained in 17% yield from methyl bicyclo[1.1.0]butane-1-carboxylate[11] (**6b**). Lower solubility in the reaction mixture may account for the poorer yield of the methyl derivative.

Cyclobutane derivatives containing a *gem*-dinitro group have not been prepared previously. Oxidative nitration[12] of the anions of mononitrocyclobutane **4e** and esters **4a** and **4b** with potassium ferrocyanide and sodium persulfate in the presence of sodium nitrite gave 1,1-dinitrocyclobutane (**8e**), ethyl 3,3-dinitrocyclobutanecarboxylate (**8a**), and diethyl 3,3-dinitrocyclobutane-1,1-dicarboxylate (**8b**) in 78%, 75%, and 78% yields, respectively, as shown in Scheme III. Acid hydrolysis of the esters **8a** and **8b** gave the corresponding acids 3,3-dinitrocyclobutanecarboxylic acid (**9a**) and 3,3-dinitrocyclobutane-1,1-dicarboxylic acid (**9b**) in 93% and 52% yields. The mono acid **9a** was converted to 3,3-dinitrocyclobutylammonium hydrochloride (**10**) in 84% yield by the Curtius reaction of the acid chloride with sodium azide followed by hydrolysis of the isocyanate with refluxing methanolic aqueous hydrochloric acid.

Reaction of the disodium salt of 1,3-dinitro derivative **4f** with silver nitrate and sodium nitrite[13] gave a (3:2) mixture of 1,1,3,3-tetranitrocyclobutane (**8f**) and 1,1,3-trinitrocyclobutane (**11**) from which **8f** was isolated in 38% yield by fractional crystallization. The instability of the disodium salt of **4f** above 5 °C or in concentrated base solutions prevents the use of the ferrocyanide oxidative nitration procedure. However, reaction of the dinitro esters **7a** and **7b** with silver nitrate and sodium nitrite in sodium carbonate solution gave **8f** directly in 21% yield. A trace amount of the trinitro derivative **11** was detected, but the formation of ethyl 1,3,3-trinitrocyclobutanecarboxylate was not observed.

Tetranitrocyclobutane **8f** has a density of 1.83 by silver nitrate flotation and single-crystal X-ray analysis and is thermally stable to its melting point of 165 °C. In alkaline ethanolic solutions, **8f** is rapidly degraded to water-soluble fragments.

1,1,3-Trinitrocyclobutane **11** was unstable and could not be isolated in a pure form. In basic aqueous solution, it decomposed rapidly. Oxidation of dinitroamine **10** with *m*-chloroperbenzoic acid gave **11**, which could not be isolated without decomposition. Attempts to convert **11** to **8f** by oxidative nitration using mildly alkaline solutions with silver, potassium ferricyanide, or tetranitromethane catalysis were unsuccessful.

Several unsuccessful attempts were made to prepare 1,2-dinitrobicyclo[1.1.0]butane from **4f**. The 1,3-dinitro-

(8) Corey, E. J.; Estreicher, H. *Tetrahedron Lett.* **1980**, *21*, 1117.
(9) Compound **4e** (bp 55–60 °C/20 mm) was identical with that prepared from cyclobutanone oxime (lit.[2] bp 70 °C/40 mm).
(10) Vasin, V. A.; Bolusheva, I. Y.; Tanaseichek, B. S. *Zh. Org. Khim.* **1986**, *22*, 670.
(11) (a) Wiberg, K.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749. (b) Wiberg, K. B.; Lampman, G. M. *J. Am. Chem. Soc.* **1966**, *88*, 4429.
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(13) Kaplan, R. B.; Shechter, H. *J. Am. Chem. Soc.* **1961**, *83*, 3535.

cyclobutane **4f** was unstable in concentrated aqueous base but was reisolated in 85% yield from dilute sodium hydroxide by acidification after 24 h. The reaction of nitronate ions with silver salts and sodium persulfate, known to give dimers,[14] did not give internal coupling with **4f** dianion. The bromination of **4f** gave only 1,3-dibrmo-1,3-dinitrocyclobutane (**5**). Unlike 1-bromo-1-nitrocyclobutane which reacts with *n*-butyllithium to give the coupled product 1,1'-dinitrobicyclobutyl,[15] the analogous reaction of **5** with molar amounts of *n*-butyllithium did not lead to nitrobicyclo[1.1.0]butane derivatives.

The dinitrodispiro compound **4c** was found to undergo potassium ferricyanide catalyzed oxidative nitration to give 5,5,10,10-tetranitrodispiro[3.1.3.1]decane (**12**) in 64% yield. The observed yield in this hindered cyclobutane derivative is in the range of expected yields for unhindered nitroalkanes.

Experimental Section[16]

2,5,8,10-Tetraoxodispiro[3.1.3.1]decane (1d). To a stirred solution of 3-methylenecyclobutanecarboxylic acid chloride[5] (21.8 g, 0.167 mmol) in 1:1 ether–benzene (250 mL) was added dry triethylamine (27.0 g, 0.267 mol) under an argon atmosphere. The resulting cream-colored suspension was stirred, refluxing for 24 h, and washed with ice cold 1 M aqueous HCl. The aqueous phase was extracted with ether (2 × 25 mL), and the combined organic layers were washed with 1 M aqueous $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated to give a reddish oil. This oil was extracted with hot hexanes (3 × 50 mL), the solvent was evaporated, and the residue chromatographed (silica gel, 5:1 hexane–ether) to give 7.9 g (50%) of 2,8-dimethylene-5,10-dioxodispiro[3.1.3.1]decane: mp 112–113 °C; IR 2970, 1765, 1690 cm^{-1}; NMR δ 3.16 (t, 8 H, J = 3 Hz), 4.83 (t, 4 H, J = 3 Hz). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.51; H, 6.32.

A solution of 2,8-dimethylene-5,10-dioxodispiro[3.1.3.1]decane (0.48 g, 2.55 mmol) in CH_2Cl_2 (50 mL) was chilled to −78 °C, and a stream of ozone in oxygen was introduced via a glass-fritted bubbler using a Welsbach ozonater (T-23). The ozonolysis was continued until the persistent blue color of dissolved ozone was observed (ca. 10 min). Dimethyl sulfide (1 mL) was added, and the solution was warmed slowly to room temperature, washed with water (2 × 25 mL), dried, and concentrated. The resulting solid was triturated with ether (2 × 50 mL) and dried to give 0.27 g (55%) of **1d**, which slowly decomposed at −15 °C: mp 215–220 °C dec; IR (KBr) 3050, 1780, 1745 cm^{-1}; NMR (DMSO-d_6) δ 3.53 (s). Anal. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 61.99; H, 4.32. Tetraoxime hemihydrate **2d**: mp 275 °C dec; IR (KBr) 3170, 2930, 1400, 960, 910 cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$) δ 3.10 (br s), 3.30 (br s), 10.35 (s, D_2O ex), 10.80 (s, D_2O ex). Anal. Calcd for $C_{10}H_{13}N_4O_{4.5}$: C, 45.97; H, 5.01. Found: C, 46.07; H, 5.11.

Diethyl 3-Chloro-3-nitrocyclobutane-1,1-dicarboxylate (3b). To a solution of diethyl 3-oximinocyclobutane-1,1-dicarboxylate[6] (**2b**) (22.8 g, 99.5 mmol) in CH_2Cl_2 (150 mL) at 0 °C was added chlorine gas until a dark green coloration persisted. The solution was concentrated on a rotary evaporator, and benzene (200 mL), tetra-*n*-butylammonium hydrogen sulfate (10.0 g, 29 mmol), and bleach (5.2% NaOCl, 250 mL) were added successively. After the mixture was stirred for 2 h, the separated aqueous layer was extracted with ether (2 × 100 mL), and the combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), concentrated, and distilled to give 20.8 g (75%) of **3b**: bp 105–110 °C (0.2 mm); IR 3650, 3080, 3030, 1725, 1560 cm^{-1}; ^1H NMR δ 1.35 (t, 6 H, J = 7 Hz), 3.40 (AB quartet, 4 H), 4.35 (q, 4 H, J = 7 Hz). Anal. Calcd for $C_{10}H_{14}ClNO_6$: C, 42.95; H, 5.05. Found: C, 43.13; H, 5.15.

5,10-Dichloro-5,10-dinitrodispiro[3.1.3.1]decane (3c). A mixture of 5,10-dioximinodispiro[3.1.3.1]decane[17] (**2c**) (1.09 g, 5.61 mmol) in benzene (35 mL) and pH 5.5 bleach (5.25% NaOCl, 25 mL) was stirred for 1.5 h. The benzene layer was separated and added to pH 10.5 bleach (5.25% NaOCl, 50 mL) and tetra-*n*-butylammonium hydrogen sulfate (1.90 g, 5.60 mmol), and the mixture was stirred for 1 h. The aqueous layer was extracted with ether (2 × 50 mL), and the combined organic layers were washed with saturated NaCl solution (25 mL), dried ($MgSO_4$), and concentrated to give a semisolid product, which was recrystallized from CH_2Cl_2–hexanes and sublimed (100 °C/0.5 mm) to give 1.5 g (90%) of **3c**: mp 171–173 °C; IR 1560, 1340 cm^{-1}; NMR δ 1.80 (m, 12 H). Anal. Calcd for $C_{10}H_{12}Cl_2N_2O_4$: C, 40.70; H, 4.10; N, 9.49. Found: C, 41.07; H, 4.20; N, 9.26.

Ethyl 3-Nitrocyclobutanecarboxylate (4a). A slow stream of chlorine gas was bubbled into a stirred solution of ethyl 3-oximinocyclobutanecarboxylate[6] (8.00 g, 50.9 mmol) in CH_2Cl_2 (50 mL) at 0 °C until the initially blue solution became blue-green. Excess chlorine and solvent were removed by rotary evaporation, and benzene (100 mL), pH 10.5 bleach (5.0% NaOCl, 100 mL), and tetra-*n*-butylammonium hydrogen sulfate (5.0 g, 15 mmol) were added. This mixture was stirred at 10 °C for 1 h, the phases were separated, and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), concentrated, and distilled to give 9.45 g (89%) of ethyl 3-chloro-3-nitrocyclobutanecarboxylate (**3a**) as a mixture of isomers: bp 72–74 °C (0.3 mm); IR 17.30, 1550 cm^{-1}; ^1H NMR δ 1.40 (t, 3 H, J = 7 Hz), 3.35 (m, 5 H), 4.20 (q, 2 H, J = 7 Hz).

A solution of hydroxylamine hydrochloride (1.80 g, 25 mmol) in water (15 mL) was added to **3a** (5.00 g, 24 mmol) in THF (100 mL). Zinc dust (2.00 g, 30.6 mmol) was added portionwise with stirring over a 10-min period at 25 °C. After 1 h, water (100 mL) was added, and the mixture was extracted with ether (2 × 50 mL). The combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), concentrated, and distilled to give 3.38 g (80%) of essentially pure **4a**. An analytical sample was obtained by dispersing 1 g of the material in 10 mL of ice-cold 1 M aqueous NaOH solution. After the mixture was stirred vigorously for 1 h, it was extracted with CH_2Cl_2 (3 × 10 mL) and then acidified to pH 5 with acetic acid. The product was extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic phases were washed with 1 M aqueous $NaHCO_3$ solution and saturated NaCl solution. The organic phase was dried ($MgSO_4$), concentrated, and distilled to give **4a** (isomeric mixture): bp 84–87 °C (0.1 mm); IR 3050, 1735, 1550 cm^{-1}; ^1H NMR δ 1.25 (t, 3 H, J = 7 Hz), 2.80 (m, 3 H), 3.05 (m, 2 H), 4.05 (q, 2 H, J = 7 H), 4.85 (m, 1 H). Anal. Calcd for $C_7H_{11}NO_4$: C, 48.55; H, 6.40. Found: C, 48.17; H, 6.11.

5,10-Dinitrodispiro[3.1.3.1]decane (4c). Solid **2c** (4.67 g, 24.0 mmol) was added portionwise to liquid ammonia (200 mL) under argon, and methanol (20 mL, 0.49 mol) was added. Sodium (6.0 g, 0.26 mol) was added in small pieces, and a persistent blue color was noted after two-thirds of the sodium was added. After 2 h the ammonia was evaporated, the residue was diluted with water, and the mixture was extracted with ether (3 × 25 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to afford 3.73 g of an oil. This oil was diluted with 20 mL of dichloroethane, and this solution was added dropwise to a solution of 40 g (0.20 mol) of 85% *m*-chloroperbenzoic acid in refluxing dichloroethane (300 mL). After the mixture was refluxed overnight, it was cooled and filtered. The filtrate was washed twice with cold 0.1 M aqueous NaOH solution and once with saturated NaCl solution, dried ($MgSO_4$), and concentrated to give a turbid oil (7 g). This oil was added with stirring to 1 M aqueous NaOH solution (20 mL). After 1 h, the mixture was washed twice with CH_2Cl_2, and the organic layers were discarded. The aqueous layer was acidified (pH 4–5) with glacial acetic acid and extracted twice with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and concentrated. The residual oil was chromatographed on silica

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(15) Kai, Y.; Knochel, P.; Kwiatowski, S.; Dunitz, J. D.; Oth, J. F. M.; Seebach, D.; Kalinowski, H. *Helv. Chim. Acta* **1982**, *65*, 137.

(16) Melting points are uncorrected, elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, proton NMR spectra were recorded in $CDCl_3$ on a Varian T-60 spectrometer, and the chemical shifts are reported relative to TMS. Infrared spectra were recorded in CH_2Cl_2 with a Perkin-Elmer 700 spectrometer.

(17) Dioxime **2c** was prepared from dione **1c** (ref 9) in 85% yield: mp 237–239 °C; IR (KBr) 3300, 2950, 1630, 1450 cm^{-1}; ^1H NMR ($CDCl_3$–DMSO) δ 1.8–3.0 (m, 12 H), 10.4 (s, 2 H). Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.26; N, 14.42. Found: C, 61.61; H, 7.33; N, 14.16.

gel (4:1 petroleum ether–ether) to give 0.67 g (13%) of **4c**: mp 30–35 °C; bp 130–140 °C (0.1 mm) (subl); IR 1550 cm^{-1}; NMR δ 1.8–2.2 (m, 12 H), 5.05 (s, 2 H). Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.23; N, 12.38. Found: C, 52.89; H, 6.12; N, 12.13.

2,5,8,10-Tetranitrodispiro[3.1.3.1]decane (4d). Chlorine gas was introduced into a 0 °C suspension of **2d** (0.220 g, 0.872 mmol) in CH_2Cl_2 (10 mL) until a homogeneous solution was obtained. The solution was stirred for 30 min and evaporated to give a blue oil, which was dissolved in benzene (10 mL). This solution was stirred over a mixture of tetra-*n*-butylammonium hydrogen sulfate (0.50 g, 1.47 mmol) and sodium hypochlorite (10 mL of pH 10.5, 5% NaOCl) for 1 h. The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL), and the combined organic layers were washed with 1 M $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated to give a solid after two ether triturations. A solution of this solid in tetrahydrofuran (25 mL) and water (5 mL) containing hydroxylamine hydrochloride (0.42 g, 6.9 mmol) was stirred while zinc powder (0.40 g, 6.0 mmol) was added slowly portionwise over 5 min. This mixture was stirred at ambient temperature for 2 h, and then refluxed for 1 h. The mixture was diluted with water and extracted with CH_2Cl_2 (2 × 25 mL). The combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated. Column chromatography of the resulting oil on silica gel using 3:1 hexane–ethyl acetate gave 52 mg (20%) of **4d**, as a mixture of isomers: TLC (3:1 hexane–EtOAc) R_f 0.10, 0.14; mp 110–112 °C; IR (KBr) 1535, 1370 cm^{-1}; NMR (CD_3CN) δ 3.0 (d, 8 H, J = 7 Hz), 5.5 (m, 4 H). Anal. Calcd for $C_{10}H_{12}N_4O_8$: C, 37.98; H, 3.83. Found: C, 37.88; H, 3.80.

***cis*-1,3-Dinitrocyclobutane (4f).** A solution of 1,3-diaminocyclobutane[6] (0.70 g, 8.1 mmol) in 1,2-dichloroethane (6 mL) was added dropwise to a solution of *m*-chloroperbenzoic acid (9.8 g, 58 mmol) in refluxing 1,2-dichloroethane (100 mL). The mixture was refluxed for 3 h, cooled to ambient temperature, and filtered, and the solids were washed with 1,2-dichloroethane (3 × 30 mL). The combined organic fractions were washed with 5% aqueous Na_2CO_3 (2 × 25 mL) and saturated NaCl solution (2 × 25 mL) and dried ($MgSO_4$). The solvent was evaporated, and the residue was purified by bulb-to-bulb distillation at 100 °C (1.5 mm) to give 0.45 g (38%) of **4f** (50:50 cis–trans mixture by ^1H NMR): IR 15550, 1400, 1380 cm^{-1}; NMR δ 2.6–3.6 (m, 4 H), 4.74 (m, 1 H), 5.05 (m, 1 H). The mixture of isomers was chromatographed on silica gel (80:20 hexane–ethyl acetate) to give *cis*-1,3-dinitrocyclobutane: mp 72–73.5 °C; NMR δ 4.78 (dd, 2 H, J = 8 Hz, 8 Hz), 3.26 (m, 4 H). Anal. Calcd for $C_4H_6N_2O_4$: C, 32.88; H, 4.14; N, 19.18. Found: C, 32.83; H, 4.12; N, 19.06.

1,3-Dibromo-1,3-dinitrocyclobutane (5). A solution of sodium carbonate (0.22 g, 2.04 mmol) in water (5 mL) was stirred with **4f** (0.23 g, 0.76 mmol) at 5 °C for 30 min, and bromine (0.35 g, 2.2 mmol) was added over 10 min. The mixture was stirred for an additional 15 min at 5 °C and filtered. The solid was washed with water and dried in air to give 0.23 g (74%) of **5** (50:50 cis–trans mixture): mp 94–117 °C; IR 1575, 1350, 1140, 1110 cm^{-1}; NMR δ 4.20 (s, trans isomer), 4.60, 3.60 (AB quartet, J = 16 Hz, cis isomer). Anal. Calcd for $C_4H_4Br_2N_2O_4$: C, 15.79; H, 1.31; N, 9.20. Found: C, 16.11; H, 1.43; N, 9.37.

Ethyl 1,3-Dinitrocyclobutane-1-carboxylate (7a). A solution of ethyl bicyclo[1.1.0]butane-1-carboxylate[11] (**6a**) (2.47 g, 19.6 mmol) in anhydrous ether (35 mL) was cooled to −20 °C, and N_2O_4 (2.02 g, 22 mmol) in ether (6 mL) was added dropwise. The resulting yellow-green solution was stirred for 10 min at −20 °C, and ethanol (25 mL) was added. The mixture was allowed to warm to room temperature. After 18 h, the solvent was removed, and the residue was chromatographed (silica gel, 3:1 hexanes–ether) to give 1.73 g (40%) of **7a** as a mixture of isomers. One of these isomers could be crystallized from the mixture using ether–hexane. This white solid (0.30 g, 7%) had R_f = 0.20 (2:1 hexane–ether); mp 87–89 °C; IR 1750, 1550, 1370 cm^{-1}; ^1H NMR δ 1.33 (t, 3 H, J = 7 Hz), 3.42 (m, 4 H), 4.27 (q, 2 H, J = 7 Hz), 4.93 (m, 1 H). Anal. Calcd for $C_7H_{10}N_2O_6$: C, 38.54; H, 4.62; N, 12.84. Found: C, 38.39; H, 4.99; N, 12.63.

Methyl 1,3-Dinitrocyclobutane-1-carboxylate (7b). The methyl ester **7b** was similarly prepared as a mixture of isomers in 17 yield from **6b**.[11] One of these isomers was obtained in crystalline from ether–hexane: mp 38–40 °C; TLC (2:1 hexane–ether) R_f = 0.24; IR 1750, 1550, 1365 cm^{-1}; ^1H NMR δ 3.56 (d, 2 H, J = 7 Hz), 3.60 (d, 2 H, J = 2 Hz), 3.96 (s, 3 H), 5.03 (d pent, 1 H, J = 2 Hz). Anal. Calcd for $C_6H_8N_2O_6$: C, 35.30; H, 3.95; N, 13.72. Found: C, 35.63; H, 4.01; N, 13.39.

Ethyl 3,3-Dinitrocyclobutanecarboxylate (8a). A solution of **4a** (5.66 g, 32.6 mmol) was added slowly to a stirred solution of potassium *tert*-butoxide (4.57 g, 40.8 mmol) in THF (50 mL) and ethanol (25 mL) at 25 °C. After 5 min, a solution of sodium nitrite (28.3 g, 0.41 mol) in water (50 mL) was added followed immediately by a solution of sodium persulfate (18.6 g, 78.1 mmol) and potassium ferricyanide (5.70 g, 17.3 mmol) in water (100 mL). After the solution was stirred for 1 h, it was extracted with ether (3 × 50 mL), and the combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated. The residual oil was distilled to give 3.87 g (54%) of **8a**: bp 100–103 °C (0.2 mm); IR 3050, 1735, 1560, 1335 cm^{-1}; ^1H NMR δ 1.35 (t, 3 H, J = 7 Hz), 3.37 (br s, 5 H), 4.15 (q, 2 H, J = 7 Hz). An analytical sample was obtained by redistillation through a 4-in. Vigreux column to give a fraction boiling at 102–103 °C (0.2 mm). Anal. Calcd for $C_7H_{10}N_2O_6$: C, 38.54; H, 4.62. Found: C, 38.52; H, 4.83.

3,3-Dinitrocyclobutanecarboxylic Acid (9a). A solution of **8a** (1.10 g, 5.04 mmol) and sodium hydroxide (0.30 g, 7.5 mmol) in ethanol (16 mL) and water (4 mL) was refluxed for 1 h, cooled to 5 °C, and acidified with 10% aqueous hydrochloric acid. The mixture was extracted with ether (3 × 25 mL), and the combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated to give 0.89 g (93%) of a solid. Recrystallization from ether–hexanes afforded an analytical sample of **9a**: mp 96–97 °C; IR 3050, 1710, 1560 cm^{-1}; ^1H NMR δ 3.43 (br s, 5 H), 10.2 (s, 1 H, D_2O ex). Anal. Calcd for $C_5H_6N_2O_6$: C, 31.59; H, 3.18. Found: C, 31.52; H, 3.13.

3,3-Dinitrocyclobutane-1,1-dicarboxylic Acid (9b). Hydroxylamine hydrochloride (5.60 g, 82 mmol) was added to a solution of **3b** (20.8 g, 74.4 mmol) in THF (200 mL) and water (50 mL). Zinc powder (6.30 g, 96.3 mmol) was added, portionwise, with cooling and stirring, over a 20-min period, and stirring was continued for 1 h. The mixture was diluted with water (200 mL) and extracted with ether (3 × 100 mL). The combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated. The residue was distilled to give 14.2 g (78%) of **4b**: bp 110 °C (0.1 mm); IR 1730, 1540 cm^{-1}; ^1H NMR δ 1.25 (t, 6 H, J = 7 Hz), 3.20 (d, 4 H, J = 7 Hz), 4.35 (q, 4 H, J = 7 Hz), 5.05 (pent, 1 H, J = 7 Hz).

The nitro diester **4b** (14.2 g, 57.9 mmol) was dissolved in a solution of sodium hydroxide (9.50 g, 0.237 mol) in 3:1 water–THF (240 mL) at 0 °C. Sodium nitrite (35 g, 0.51 mol) was added, and the resulting solution was poured into a solution of sodium persulfate (35 g, 0.147 mol), potassium ferricyanide (9.50 g, 28.8 mmol), and Na_2CO_3 (7.0 g, 56.4 mmol) in water (175 mL). After the solution was stirred for 1 h at 22–25 °C, it was acidified to pH 2 with cold 6 M aqueous HCl. The aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated. Trituration of the residue with hexane gave 7.06 g (52%) of **9b**: mp 179–180 °C dec; IR (KBr) 3050, 1710, 1580, 1375, 1280, 1140 cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$) δ 3.55 (s, 4 H), 8.60 (br s, 1 H). Anal. Calcd for $C_6H_6N_2O_8$: C, 30.78; H, 2.58. Found: C, 31.05; H, 2.86.

1,1-Dinitrocyclobutane (8e). A solution of nitrocyclobutane, **4e**[9] (0.60 g, 5.9 mmol), and sodium hydroxide (0.39 g, 9.6 mmol) in water (5 mL) was stirred at ambient temperature for 45 min and then cooled to 0 °C. A solution of sodium nitrite (1.67 g, 24 mmol) in water (3 mL), a solution of potassium ferricyanide (0.40 g, 1.19 mmol) in water (3 mL), CH_2Cl_2 (5 mL), and solid sodium persulfate (1.41 g, 5.9 mmol) were added. The resulting mixture was stirred at 5 °C for 15 min and at 23 °C for 1 h. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried ($MgSO_4$) and evaporated to give 0.68 g (78%) of **8e**. An analytical sample was prepared by molecular distillation (100 °C, 0.5 mm): IR (film) 3030 (m), 2945 (mw), 1562 (s), 1420 (ms) cm^{-1}; NMR δ 2.2 (m, J = 8.5 Hz, 2 H), 3.18 (t, J = 8.5 Hz, 4 H). Anal. Calcd for $C_4H_6N_2O_4$: C, 32.88; H, 4.14; N, 19.18. Found: C, 33.12; H, 4.20; N, 19.40.

3,3-Dinitrocyclobutylammonium Hydrochloride (10). A solution of **9a** (10.00 g, 52.6 mmol) in 30 mL of thionyl chloride was stirred at room temperature for 24 h. The excess thionyl

chloride was removed by rotary evaporation, and CH_2Cl_2 (100 mL) was added. The solution was cooled to 0 °C, and a solution of tetra-*n*-butylammonium chloride (150 mg, 0.54 mmol) and sodium azide (4.50 g, 69.2 mmol) in 15 mL of water was added. The two-phase mixture was stirred for 3 h at 0 °C, the phases were separated, and the organic layer was washed with water (2 × 25 mL) and dried ($MgSO_4$). IR spectrum of this solution: 2190, 1715, 1565, 1420, 1360, and 1340 cm^{-1}. Trifluoroacetic acid (8.0 g, 70 mmol) was added, and the solution was filtered and refluxed for 18 h. The cooled mixture was washed with ice-cold 1 M $NaHCO_3$ solution (25 mL), dried ($MgSO_4$), and concentrated to afford a yellow solid. Ether was added (100 mL); the mixture was filtered and concentrated to give 11.3 g (84%) of *N*-(3,3-dinitrocyclobutyl)trifluoroacetamide: mp 82–84 °C; TLC (ether) R_f = 0.10; IR 3480, 3100, 1730, 1560, 1335, 1220, 1170 cm^{-1}; ^1H NMR δ 3.50 (m, 4 H), 4.52 (m, 1 H), 7.0 (br s, 1 H). Anal. Calcd for $C_6H_6F_3N_3O_5$: C, 28.03; H, 2.35; N, 16.34; F, 22.16. Found: C, 28.01; H, 2.56; N, 16.38; F, 22.14.

To a solution of above amide (11.3 g, 44.0 mmol) in 200 mL of methanol was added 20 mL of 12 M HCl. The solution was refluxed overnight and evaporated, and the residue was triturated with ether (2 × 40 mL) to give 8.70 g (100%) of **10**: mp 215–217 °C dec; IR (KBr) 3000, 1560, 1345 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.60 (m, 5 H), 8.50 (br s, 3 H). Anal. Calcd for $C_4H_8N_3ClO_4$: C, 24.32; H, 4.08; N, 21.27; Cl, 17.94. Found: C, 24.70; H, 4.26; N, 21.31; Cl, 17.56.

1,1,3,3-Tetranitrocyclobutane (8f) from 4f. A mixture of **4f** (50:50 cis/trans mixture) (0.42 g, 2.8 mmol), sodium carbonate (0.90 g, 8.5 mmol), and sodium nitrite (1.18 g, 17 mmol) was dissolved in water (25 mL) at 10 °C. After 20 min, the mixture was diluted with water (20 mL) and filtered, and ether (25 mL) was added. Then, a solution of silver nitrate (3.68 g, 21.7 mmol) in water (10 mL) was added, followed by a 10% NaOH solution (10 drops), and the mixture was stirred at 10 °C for 20 min and at room temperature for 20 min. The mixture was filtered through Celite. The aqueous layer was extracted with ether (3 × 40 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated to give 0.55 g of a mixture of 1,1,3-trinitrocyclobutane (**11**) and 1,1,3,3-tetranitrocyclobutane **8f** (2: 3 by ^1H NMR analysis). Recrystallization of this mixture from CH_2Cl_2–chloroform gave 0.25 g (38%) of **8f** as a colorless solid: mp 165–166 °C; d = 1.825 ($AgNO_3$ flotation); d = 1.83 (single-crystal X-ray[18]); IR 3000, 1595, 1400, 1365, 1330 cm^{-1}; NMR (acetone-d_6) δ 4.83 (s). Anal. Calcd for $C_4H_4N_4O_8$: exact mass (M′ – $2NO_2$), 144.0169; C, 20.35; H, 1.71. Found: exact mass, 144.0171; C, 20.47; H, 1.78.

8f from 7a. To a stirred solution of **7a** in 3:1 water–THF (140 mL) at 0 °C was added NaOH (2.70 g, 67.5 mmol). After 15 min, sodium nitrite (7.7 g, 0.11 mol) was added, and the mixture was stirred for 5 min. Ether (100 mL) and a solution of silver nitrate (19.0 g, 0.112 mol) in 100 mL of water were added, and the resulting mixture was stirred for 1 h at 0 °C and at ambient temperature for 2 h. Aqueous saturated NaCl (50 mL) was added, the suspension was filtered, and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated to give a semisolid. Repeated trituration with ether–hexanes and washing with cold anhydrous ether gave 1.14 g (21%) of **8f**: mp 165–166 °C, identical with that prepared above.

5,5,10,10-Tetranitrodispiro[3.1.3.1]decane (12). A mixture of 1 M aqueous NaOH (10 mL), dioxane (3 mL), and **4c** (0.20 g, 0.88 mmol) was stirred at 20 °C until it was homogeneous (15 min), and solid sodium nitrite (1.2 g, 17 mmol) was added. After 5 min, a mixture of sodium persulfate (1.26 g, 5.30 mmol) and potassium ferricyanide (0.35 g, 1.0 mmol) was added in one portion. The resulting red-amber solution was stirred at 20 °C for 3 h, and then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated to afford 0.21 g of a solid, which was sublimed (95 °C/0.10 mm) to give 0.10 g (64%) of **12**: mp 179–180 °C; IR 1575 cm^{-1}; NMR δ 2.20 (m, 4 H), 2.65 (m, 8 H); d = 1.52 g/cm^3; ($AgNO_3$ flotation). Anal. Calcd for $C_{10}H_{12}N_4O_8$: C, 37.98; H, 3.82; N, 17.72. Found: C, 38.32; H, 3.84; N, 17.57.

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Registry No. **1d**, 120525-63-5; **2a**, 98431-84-6; **2b**, 100132-82-9; **2c**, 120525-64-6; **2d**, 120525-65-7; *cis*-**3a**, 120525-66-8; *trans*-**3a**, 120525-67-9; **3b**, 120525-68-0; **3c**, 120525-69-1; **3d**, 120525-70-4; *cis*-**4a**, 120525-71-5; *trans*-**4a**, 120525-72-6; **4b**, 120525-73-7; **4c**, 120525-74-8; **4d**, 120525-75-9; **4e**, 2625-41-4; *cis*-**4b**, 120525-76-0; *trans*-**4b**, 120525-77-1; *cis*-**5**, 120525-78-2; *trans*-**5**, 120525-79-3; **6a**, 29820-55-1; **6b**, 4935-01-7; *cis*-**7a**, 120525-80-6; *trans*-**7a**, 120525-81-7; *cis*-**7b**, 120525-82-8; *trans*-**7b**, 120525-83-9; **8a**, 120525-84-0; **8e**, 120525-85-1; **8f**, 120167-77-3; **9a**, 120167-76-2; **9b**, 120181-39-7; **10**, 120525-86-2; **11**, 120167-75-1; **12**, 120525-88-4; 3-methylenecyclobutanecarboxylic acid chloride, 98198-78-8; 2,8-dimethylene-5,10-dioxodispiro[3.1.3.1]decane, 120525-62-4; 1,3-diaminocyclobutane, 91301-66-5; *N*-(3,3-dinitrocyclobutyl)-trifluoroacetamide, 120525-87-3.

(18) X-ray structure of **8f** will published elsewhere. Gillardi, R. Naval Research Laboratory, private communication.

A New Method for Synthesis of Trifluoromethyl-Substituted Phenols and Anilines

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Triethyl(trifluoromethyl)silane and tri-*n*-butyl(trifluoromethyl)silane were found to react with quinones by addition to one of the carbonyl carbon atoms, giving dienones containing geminal trifluoromethyl and trialkylsiloxy substituents. These reactions were catalyzed by a variety of basic compounds. Quinones found to undergo this process include 1,2- and 1,4-benzoquinones (some bearing alkyl substituents), naphthoquinone, anthraquinone, and phenanthrenequinone. Most of the resulting dienones gave (trifluoromethyl)phenols on dissolving metal reduction, and one was subjected to reductive amination to give (trifluoromethyl)aniline.

The trifluoromethyl group is an increasingly popular aromatic substituent in compounds synthesized for biological applications. Still, only a handful of methods exist for its introduction into aromatic compounds. Classic methods such as conversion of methyl groups by photochlorination followed by hydrofluoric acid treatment[1] or

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