of 0.72 g/mL and therefore was 3.9 M in both cyclopentane and cylohexane. Solution B had a density of 0.85 g/mL and was therefore 1.75 M in each of the aromatic hydrocarbons present. Solution C consisted of *n*-pentane (3.6 g, 0.050 mol), *c*-pentane (3.5 g, 0.050 mol), *cis*-decalin (6.9 g, 0.50 mol), and *trans*-decalin (6.9 g, 0.050 mol). Solution D consisted of toluene (9.2 g, 0.10 mol), *p*-xylene (10.6 g, 0.10 mol), and naphthalene (6.4 g, 0.050 mol). Solution C had a density of 0.81 g/mL and was therefore 1.9 M in each of the hydrocarbons present. Solution D had a density of 0.89 g/mL and was therefore 3.4 M in toluene and *p*-xylene and 1.7 M in naphthalene.

Three U-tubes, each equipped with a Teflon-coated magnetic stirring bar, were set up so that a single magnetic stirrer would stir all three at the same rate. Equal amounts (~12 mL) of solutions I, II, and III were placed in each U-tube. Two separate experiments were then performed in succession to determine the relative rates of transfer of the various hydrocarbons through the aqueous phases. The first experiment was to place 2.0 mL of solution A and 2.0 mL of solution B on opposite sides of each of the three U-tubes already containing solutions I, II, and III. Stirring was then commenced and continued for several days. The stirring rate was controlled so that no vortexing occurred.

The same experiment was also performed with solution C and D being used in place of A and B, respectively. After being stirred for several days, the organic solutions were analyzed by GLPC to determine the quantities of each organic compound which was transported through the aqueous phase. The relative rates of transport of each of the organic compounds are listed in Table I. The unfacilitated rate of transport of cyclopentane through aqueous KOH was given the arbitrary value of 1.0.

Registry No. 1, 1129-90-4; 2, 6573-73-5; 3, 65975-29-3; 4, 102652-58-4; 9, 102652-59-5; 10, 102682-72-4; 11, 7215-74-9; 12, 102652-60-8; 13, 43135-91-7; 14, 3705-86-0; 15, 102652-61-9; 16, 102652-62-0; 17, 102682-73-5; 18, 102652-63-1; 19, 102682-74-6; 1,1-dichlorocyclododecane, 60223-10-1; cyclododeca-1,2-diene, 1129-91-5; 1,1-dichlorocyclopentadecane, 102652-64-2; cyclopentadecanone, 502-72-7; cyclododecane-1,2-dione, 3008-41-1; *o*-phenylenediamine, 95-54-5; diethyl 5,6-dinitrobenzimidazolone-1,3-di-α-acetate, 1848-95-9.

Synthesis of Polynitro Compounds. Hexasubstituted Benzenes

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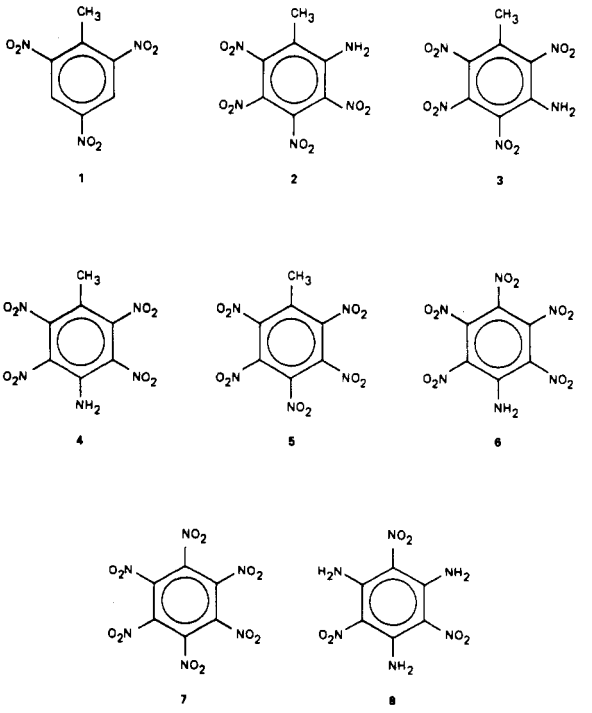
The synthesis of the three isomeric aminotetranitrotoluenes by nitration of an appropriate aminodinitrotoluene is presented, and the apparent ipso nitration of 4-amino-2,6-dinitrotoluene to give pentanitroaniline is also discussed. The oxidation of the isomeric aminotetranitrotoluenes to pentanitrotoluene is described, as is the ammonolysis of pentanitroaniline and of pentanitrotoluene.

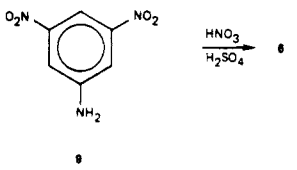
Our continuing interest in highly nitrated species, energetic materials which have explosive and propellant applications, has prompted us to investigate methods of preparation of pernitrated aromatic systems.[2-5] Polynitroaromatic analogues of 2,4,6-trinitrotoluene (TNT, 1) and polyaminopolynitroaromatic compounds are expected to show improved properties of density, power, sensitivity and stability, but few of these species have been synthesized. This study deals, then, with the synthesis and reactions of the isomeric 2-amino-3,4,5,6-, 3-amino-2,4,5,6-, and 4-amino-2,3,5,6-tetranitrotoluenes (**2**, **3**, and **4**) and their oxidation to 2,3,4,5,6-pentanitrotoluene (**5**). We also discuss the apparent ipso nitration of **4** to 2,3,4,5,6-pentanitroaniline (**6**) from which hexanitrobenzene (**7**) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, **8**) may be prepared.

Successive direct nitration by electrophilic substitution of an aromatic ring system, of course, becomes progressively more difficult due to the deactivating influence of the nitro groups already in place. Such difficulties can, however, be overcome by the stategic inclusion of a suitable activating group, as exemplified by the Flürscheim synthesis of **6** from 3,5-dinitroaniline, **9**.[6]

Chart I



(1) Formerly at Materials Reasearch Laboratories, P.O. Box 50, Ascot Vale, Victoria 3032, Australia.
(2) Nielsen, A. T.; Atkins, R. L.; Norris, W. P. *J. Org. Chem.* **1979**, *44*, 1181.
(3) Nielsen, A. T.; Atkins, R. L.; Norris, W. P.; Coon, C. L.; Sitzmann, M. E. *J. Org. Chem.* **1980**, *45*, 2341.
(4) Atkins, R. L.; Nielsen, A. T.; Bergens, C; Wilson, W. S. *J. Org. Chem.* **1984**, *49*, 503.
(5) Nielsen, A. T.; Norris, W. P.; Atkins, R. R.; Vuono, W. R. *J.* Org. Chem. **1983**, *48*, 1056.



9

Our synthesis strategy was to use the amine function in a dual capacity. The activating and directing properties of the group would make possible the hitherto inaccessible aminopolynitro compounds. Subsequent oxidation of the amine group by peroxydisulfuric acid using methods developed in our laboratory would lead to pernitrated systems.

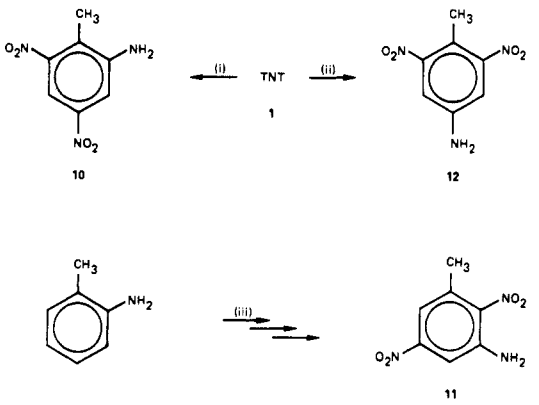
The isomeric 2-amino-4,6-, 3-amino-2,5-, and 4-amino-2,6-dinitrotoluenes (**10**, **11**, and **12**) were selected as appropriate precursors for the synthesis of the corresponding aminotetranitrotoluenes **2**, **3**, and **4**. 4-Amino-2,6-dinitrotoluene (**12**) was prepared by selective reduction of TNT using hydrogen sulfide and ammonium hydroxide in dioxane.[7] Reduction of TNT using iron in acetic acid, followed by fractional crystallization from ethanol, afforded **10**.[8] 3-Amino-2,5-dinitrotoluene (**11**) was prepared in several steps from *o*-toluidine (Scheme I).[7]

Nitration of the isomeric aminodinitrotoluenes proved more complex than expected and involved some interesting chemistry. Attempts to prepare **4** by treatment of **12** with mixed acid at elevated temperature resulted instead in an apparent ipso nitration to give pentanitroaniline (**6**) in 50–55% yield (Scheme II). However, NMR studies and mass spectral analysis of effluent gases indicated that **6** was formed by ring nitration at the 3- and 5-positions, followed by expulsion of the methyl group as carbon dioxide—presumably via an intermediate benzoic acid. Methyl sulfate could not be detected in the reaction mixture, while carbon dioxide was identified as a reaction product in the effluent gas. Subsequently, we showed that nitration of **4** under the same conditions also gave **6**, while attempts to prepare 4-amino-2,3,5,6-tetranitrobenzoic acid (**14**) by nitration of 4-amino-2,6-dinitrobenzoic acid (**13**) also gave **6** as the major reaction product.[9]

This unexpected reaction, coupled with the oxidation of **6** in oleum solution to hexanitrobenzene (**7**) using peroxydisulfuric acid prepared in situ using 98% hydrogen peroxide[2,3] or ozone gas,[4] allows the synthesis of **7** from cheap, readily available TNT (Scheme III). Further, treatment of **6** with ammonia in a variety of organic solvents results in the formation of TATB (**8**) in high yield, thereby allowing a synthetic route to that material from TNT.

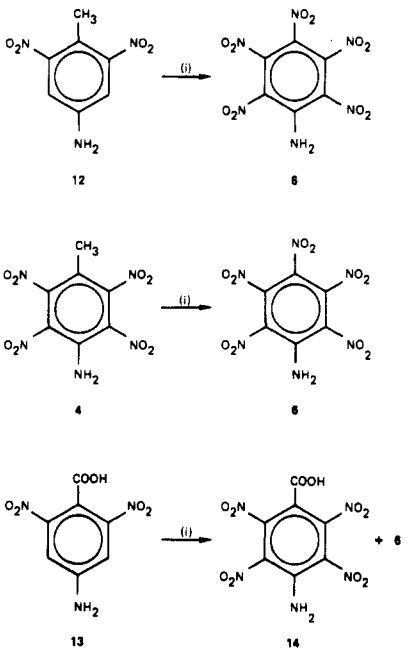
Nitration of **12** at 0 °C using 90% nitric and 96% sulfuric acids in glacial acetic acid or using nitronium tetrafluoroborate in dichloroethane at ambient temperature gave the trinitronitramine **15** as a pale yellow oil (Scheme IV). (Careful workup was required to avoid conversion to the sensitive diazophenol **16**; this reaction is discussed in some detail in a recent paper.[10] As pointed out by one referee, diazophenol formation can frequently be inhibited by the presence of urea or sulfamic acid.) Dissolution of **15** in 96% sulfuric acid and stirring at 0 °C or ambient temperature for 2 days resulted in nitramine rearrangement to **4** in 35% overall yield from **12**.

Scheme I[a]



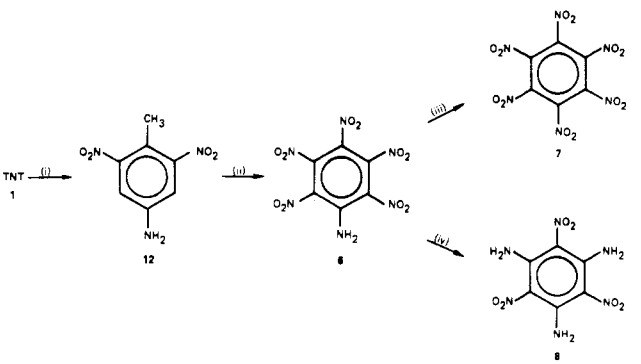
[a] (i) Fe/AcOH; (ii) H_2S/NH_4OH/dioxane; (iii) six steps.

Scheme II[a]



[a] (i) HNO_3/H_2SO_4/70 °C.

Scheme III[a]

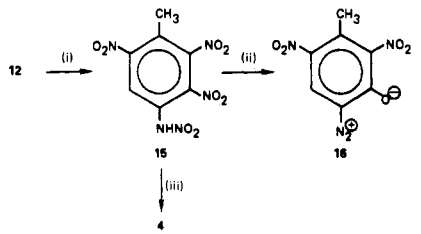


[a] (i) H_2S/NH_4OH/dioxane; (ii) HNO_3/H_2SO_4/70 °C; (iii) H_2O_2 or O_3/oleum; (iv) NH_3/toluene/CCl_4.

A much improved synthesis of **4** was achieved by nitration of **12** at ambient temperature using 90% nitric acid in 96% sulfuric acid to give the tetranitronitramine **17** as a pale yellow solid. Suspension of **17** in 96% sulfuric acid and stirring with anisole at ambient temperature resulted in cleavage of the nitramine to give **4** in 75% overall yield

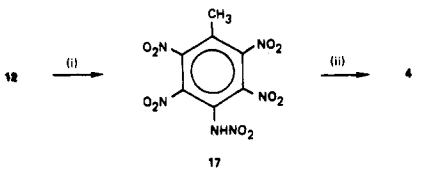
(6) Flürscheim, B.; Holmes, E. L. *J. Chem. Soc.* **1928**, 3041.
(7) Nielsen, A. T.; Henry, R. A.; Norris, W. P.; Atkins, R. L.; Moore, D. W.; Lepie, A. H.; Coon, C. L.; Spanggord, R. J.; Son, D. V. H. *J. Org. Chem.* **1979**, *44*, 2499.
(8) Wulfman, D. S.; Cooper, C. F. *Synthesis* **1978**, *12*, 924.
(9) Nielsen, A. T.; Chafin, A. P., unpublished results.
(10) Atkins, R. L.; Wilson, W. S. *J. Org. Chem.* **1986**, *51*, 2572.

Scheme IV[a]



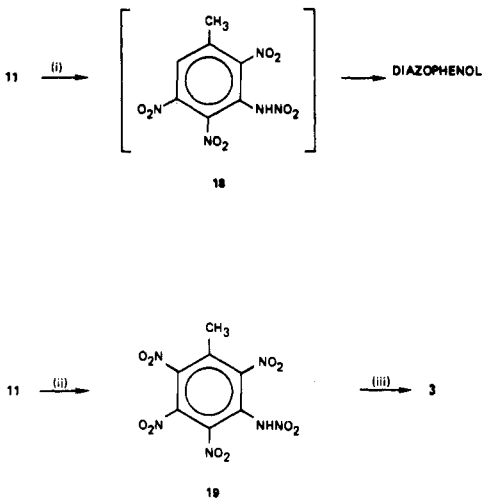
[a] (i) $HNO_3/H_2SO_4/AcOH/0$ °C or $NO_2BF_4/C_2H_4Cl_2$/ambient; (ii) CH_2Cl_2, reflux; (iii) H_2SO_4.

Scheme V[a]



[a] (i) HNO_3/H_2SO_4/ambient; (ii) C_6H_5OMe/H_2SO_4/ambient.

Scheme VI[a]



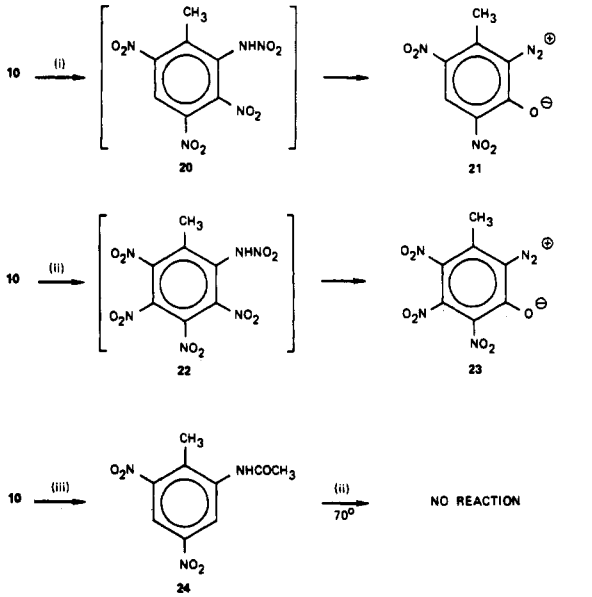
[a] (i) $HNO_3/H_2SO_4/AcOH$; (ii) HNO_3/H_2SO_4/ambient; (iii) C_6H_5OMe/H_2SO_4/ambient.

from **12** (Scheme V). The rationale for this cleavage was the equilibrium of aromatic nitramines in strong acid solution with the amine and nitronium ion (and/or related radical species)[11] and the expectation that the equilibrium could be shifted by the presence of a strong nucleophile such as anisole to react with the nitronium ion.

Nitration of **11** at 0 °C using mixed acid in glacial acetic acid gave a dinitrodiazophenol, presumable via the intermediate trinitronitramine **18**.[12] No trace of **18** was detected in the reaction mixture (Scheme VI). Further, the precise structure of the product could not easily be determined, and due to its explosive sensitivity, this route was abandoned. Nitration of **11** at ambient temperature using 90% nitric acid in 96% sulfuric acid gave the desired tetranitronitramine **19**, which was also cleaved by reaction with anisole in 96% sulfuric acid at ambient temperature, giving **3** in 46% yield from **11**.

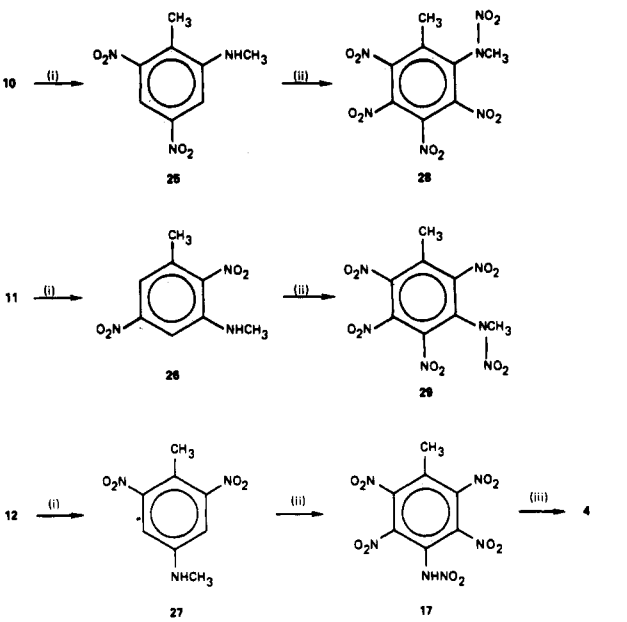
Initial attempts at nitration of **10** under a variety of conditions gave one or the other of the diazophenols **21** and **23** rather than the desired nitramines **20** and **22**

Scheme VII[a]



[a] (i) $HNO_3/H_2SO_4/AcOH$; (ii) HNO_3/H_2SO_4; (iii) AcCl/pyridine.

Scheme VIII[a]



[a] (i) $CH_2O/H_2SO_4/120$ °C; (ii) $HNO_3/H_2SO_4/0$ °C; (iii) C_6H_5OMe/H_2SO_4.

(Scheme VII). These diazophenols were presumed to be formed from the nitramines as described by Scilly;[12] therefore, the amine functionality was protected in an attempt to inhibit this rearrangement. Acetylation of **10** using acetyl chloride and pyridine gave the amide **24**. However, attempted nitration of **24**, even using mixed acid at 70 °C, resulted in no reaction.

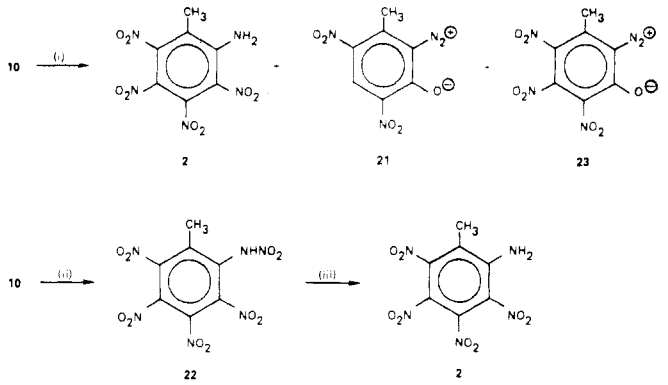
Methylation of **10** using paraformaldehyde in 96% sulfuric acid at 120 °C[13] gave the *N*-methyl derivative **25** (Scheme VIII). Treatment of **11** and **12** in a similar fashion afforded the corresponding isomers **26** and **27**. Nitration of **25** at 0 °C using 90% nitric acid in 96% sulfuric acid gave the pentanitro-*N*-methylaminotoluene

(11) White, W. N. In *Mechanisms of Molecular Migrations*; Thyagarian, B. S., Ed.; Wiley-Interscience: New York 1971; Vol. 3, pp 109–143.

(12) Mudge, P. R.; Salter, D. A.; Scilly, N. R. *J. Chem. Soc., Chem. Commun.* **1975**, 509.

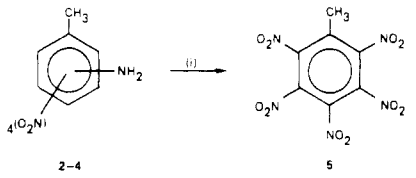
(13) Halasy, A. *Chem. Ind. (London)* **1969**, 1701.

Scheme IX[a]



[a] (i) 4 equiv 100% HNO_3/90–100% H_2SO_4/ambient; (ii) HNO_3/80% H_2SO_4; (iii) C_6H_5OMe/H_2SO_4.

Scheme X[a]



[a] (i) H_2O_2/oleum.

28 in 35% yield, while treatment of **26** in a like manner gave a 47% yield of the isomeric **29**. However, nitration of **27** under the same conditions gave **17**, identified by spectral comparison with material prepared directly from **12** and characterized by cleavage with anisole in sulfuric acid to give the amine **4**.

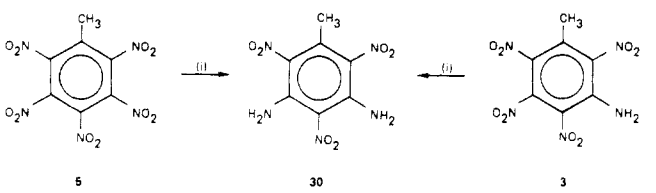
Returning to attempts to synthesize **2**, nitration of **10** using 90% nitric acid and 96% sulfuric acid in glacial acetic acid either at ambient temperature or at 0 °C gave only **21** (Scheme VII). However, nitration of **10** using 4 equiv of 100% nitric acid in 90–100% sulfuric acid at ambient temperature gave up to 22% of **2**, together with a mixture of the diazophenols **21** and **23** (Scheme IX). A much improved synthesis of **2** was realized by nitrating **10** in 80% sulfuric acid with use of 90–100% nitric acid to give the nitramine **22**, which was cleaved with anisole in 96% sulfuric acid to give **2** in 48% overall yield from **10**.

Pentanitrotoluene (**5**) was first prepared (Scheme X) by oxidation of 3,5-bis(diacetylamino)-2,4,6-trinitrotoluene using peroxydisulfuric acid.[3] However, the synthesis of the isomeric aminotetranitrotoluenes offers an alternative synthesis of **5** (Scheme XI). Indeed, each isomer was oxidized to **5** in approximately 80% yield by treatment at ambient temperature with 85–98% hydrogen peroxide in 20% oleum. Further, **5** may also be prepared by bubbling ozone gas through a solution of **4** in oleum.[4]

The reaction of hexanitrobenzene (**7**) with ammonia in methylene chloride to give TATB (**8**) has been previously documented,[3] while conversion of pentanitroaniline (**6**) to TATB in the same way is described in this paper. In a similar vein, pentanitrotoluene **5** also reacts with ammonia in *p*-dioxane to form 3,5-diamino-2,4,6-trinitrotoluene (**30**), as indeed does 3-amino-2,4,5,6-tetranitrotoluene (**3**).

The isomeric aminotetranitrotoluenes have, then, been prepared by nitration of the appropriate aminodinitrotoluenes and by cleavage of the resultant nitramines using anisole in sulfuric acid. Furthermore, nitration of 4-amino-2,6-dinitrotoluene under more forcing conditions leads to pentanitroaniline. Pentanitrotoluene and hexanitrobenzene have been prepared by oxidation of these amines using peroxydisulfuric acid, while 3,5-diamino-

Scheme XI[a]



[a] (i) NH_3/dioxane.

2,4,6-trinitrotoluene and 1,3,5-triamino-2,4,6-trinitrobenzene have been obtained by ammonolysis. Thus, a range of new energetic materials is accessible from the readily available TNT. The properties of these materials will be discussed elsewhere.

Experimental Section

WARNING! Polynitroaromatics are powerful explosives, while diazophenols are sensitive to friction, heat, and impact; all should be handled with extreme caution.

Satisfactory elemental analyses were obtained for new compounds by Galbraith Laboratories, Knoxville, TN; all previously known compounds were spectrally identical with authentic materials prepared by established procedures. Melting points were determined in capillary tubes using a Büchi 510 melting point apparatus. Infrared spectra were recorded as potassium bromide disks using a Perkin-Elmer Model 137 spectrophotometer. Proton magnetic resonance spectra were recorded with a Varian EM-360 spectrometer, using samples of 2–5% concentration in acetone-d_6 or chloroform-*d* with tetramethylsilane as an internal standard.

Pentanitroaniline (6). 4-Amino-2,6-dinitrotoluene (**12**)[7] (1.00 g, 5.1 mmol) was dissolved in 96% sulfuric acid (40 mL) at ambient temperature. Ninety percent nitric acid (3 mL) was added over 2 min with stirring, and the stirred solution was slowly heated to 80 °C over 2 $^1/_2$ h. The solution was cooled to ambient temperature and extracted with dichloromethane (4 × 50 mL). The extract was dried over anhydrous magnesium sulfate and was evaporated to dryness to give a bright yellow solid (0.75 g, 47%, mp 195–200 °C dec) identified on the basis of IR and NMR spectra as pentanitroaniline (**6**).[3,4,6]

1,3,5-Triamino-2,4,6-trinitrobenzene (8). Pentanitroaniline (**6**) (recrystallized from dichloroethane to give a solid with mp 204–207 °C) (1.0 g, 3.1 mmol) was dissolved in a 1:1 mixture of toluene and carbon tetrachloride (250 mL); then anhydrous ammonia was bubbled through the solution for 35 min. Filtration and drying at the pump gave a yellow solid (0.79 g, 97%, does not melt below 365 °C) identified by IR as 1,3,5-triamino-2,4,6-trinitrobenzene (**8**).[14]

4-Amino-2,3,5,6-tetranitrotoluene (4). Method A. 4-Amino-2,6-dinitrotoluene (**12**)[7] (0.60 g, 3.0 mmol) was dissolved in a mixture of glacial acetic acid (12 mL) and 96% sulfuric acid (36 mL) at 0 °C; 90% nitric acid (1.8 mL) in glacial acetic acid (12 mL) was added dropwise with stirring at the same temperature. After being stirred at 0 °C for 5 h, the mixture was placed in a freezer overnight (1–10 °C) and then stirred at 0 °C for a further 4 h. Extracting with dichloromethane (4 × 50 mL), washing the extract with water (2 × 100 mL), drying over anhydrous magnesium sulfate, and evaporating to dryness gave a pale yellow oil (0.68 g, 78%) (IR (KBr) 3350 (NH) and 1630 cm^{-1} (NO_2); NMR (acetone-d_6) δ 8.53 (s, 1, ArH) and 2.57 (s, 3, CH_3)), identified as 4-amino-*N*,2,3,6-tetranitrotoluene (**15**), which due to its instability was used immediately without purification. The crude nitramine **15** (0.68 g) was dissolved in 96% sulfuric acid (100 mL) and maintained at 0 °C for 2 $^1/_2$ days. The solution was poured on ice (ca. 250 g) and the mixture was extracted with dichloromethane (2 × 150 mL) and chloroform (2 × 150 mL). the combined extracts were dried over anhydrous magnesium sulfate and evaporated to leave a yellow solid. Recrystallization from chloroform/hexane gave yellow needles (0.31 g, 35%, mp 230–235 °C) (IR (KBr) 3320 and 3420 (NH) and 1540 cm^{-1} (NO_2); NMR

(14) Jackson, C. L.; Wing, J. F. *J. Am. Chem. Soc.* **1887**, *9*, 354; **1888**, *10*, 287.

($CDCl_3$) δ 7.60 (br s, 2, NH_2) and 2.15 (s, 3, CH_3)), identified as 4-amino-2,3,5,6-tetranitrotoluene (4). Anal. Calcd for $C_7H_5N_5O_8$: C, 29.26; H, 1.76; N, 24.38. Found: C, 29.10; H, 1.71; N, 24.16.

4-Amino-2,3,5,6-tetranitrotoluene (4). Method B. 4-Amino-2,6-dinitrotoluene (**12**)[7] (0.30 g, 1.5 mmol) and nitronium tetrafluoroborate (0.48 mg, 3.6 mmol) were stirred in ethylene dichloride (50 mL) at ambient temperature for 2 h. Water (2 drops) was added and the stirring was continued for 1 h. Drying over anhydrous magnesium sulfate and evaporating the solvent gave the nitramine **15** (0.24 g, 55%), which was converted to the amine 4 in method A.

4-Amino-2,3,5,6-tetranitrotoluene (4). Method C. 4-Amino-2,6-dinitrotoluene (**12**) (1.00 g, 8.1 mmol) was dissolved in 96% sulfuric acid (40 mL) and was cooled to 5 °C. Ninety percent nitric acid (3 mL) was added dropwise with stirring over 10 min, and the reaction mixture was packed in ice and stirred overnight (16 h). The resulting yellow suspension was extracted with dichloromethane (3 × 100 mL); the extract was dried over anhydrous magnesium sulfate and was evaporated to dryness to give a fine yellow solid (1.44 g, 100%) (IR (KBr) 3000 (NH), 1550 cm^{-1} (NO_2); NMR (acetone-d_6) δ 2.70 (s, 3, CH_3) and 8.90 (br, 1, NH)) identified as 4-amino-*N*,2,3,5,6-pentanitrotoluene (**17**), which was used without further purification. The nitramine **17** (1.44 g) was suspended in 96% sulfuric acid (25 mL) and anisole (0.5 mL) was added at ambient temperature. The dark suspension was stirred at ambient temperature for 30 min and was extracted with dichloromethane (3 × 100 mL). Drying over anhydrous magnesium sulfate and evaporating to dryness gave a fine yellow solid (1.14 g, 78%) recrystallized from dichloromethane as fine yellow needles and identified as 4-amino-2,3,5,6-tetranitrotoluene (**4**).

Pentanitroaniline (6). Ninety percent nitric acid (0.7 mL) was added to 100% sulfuric acid (10 mL), and 4-amino-2,3,5,6-tetranitrotoluene (**4**) (0.15 g, 0.8 mmol) was added with stirring at ambient temperature. After being stirred at ambient temperature for 60 min, the reaction mixture was heated to 75 °C for 90 min. Cooling and extracting with dichloroethane (2 × 50 mL) followed by drying over anhydrous magnesium sulfate and evaporating to dryness gave a yellow solid (0.066 g, 40%) identified as pentanitroaniline.

3-Amino-2,4,5,6-tetranitrotoluene (3). 3-Amino-2,5-dinitrotoluene (**11**)[7] (1.0 g, 8.1 mmol) was dissolved in 96% sulfuric acid (30 mL); 90% nitric acid (3 mL) was added dropwise with stirrng at ambient temperature. The reaction mixture was stirred for 3 h and extracted with dichloromethane (4 × 50 mL). Drying over anhydrous magnesium sulfate and evaporating to dryness gave the nitramine intermediate **19** as a pale yellow oil, which was redissolved in 96% sulfuric acid (150 mL). Anisole (1.0 g) was added, and the solution was stirred at ambient temperature for 1 h. Extracting with dichloromethane (4 × 100 mL), drying over anhydrous magnesium sulfate, and evaporating to dryness gave a yellow solid, which was recrystallized from chloroform to give yellow needles (0.668 g, 46%, mp 192–193 °C) (IR (KBr) 3470 and 3370 (NH) and 1530 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 6.85 (br s, 2, NH_2) and 2.53 (s, 3, CH_3)), identified as 3-amino-2,4,5,6-tetranitrotoluene (**3**). Anal. Calcd for $C_7H_5N_5O_8$: C, 29.26; H, 1.74; N, 24.38. Found: C, 29.34; H, 1.71; N, 24.25.

***N*-Acetyl-2-amino-4,6-dinitrotoluene (24).** 2-Amino-4,6-dinitrotoluene (**10**)[10] (0.60 g, 3.0 mmol) was dissolved in pyridine (5 mL), and acetyl chloride (0.23 mL) was added. The mixture was heated under reflux for 40 min, and the bulk of the pyridine was removed by evaporation. The residue was dissolved in dichloromethane (75 mL) and washed with 5% hydrochloric acid. The organic phase was dried over anhydrous magnesium sulfate and evaporated to leave a crystalline residue, which was recrystallized from chloroform to give a cream crystalline solid (0.475 g, 65%, mp 154–156 °C) (IR (KBr) 3430 (NH), 1725 (CO), and 1530 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 9.23 (d, 1, Ar H, J = 3 Hz), 8.69 (d, 1, Ar H, J = 3 Hz) 7.5 (br s, 1, NH), 2.54 (s, 3, $ArCH_3$) and 2.35 (s, 3, NCH_3)), identified as *N*-acetyl-2-amino-4,6-dinitrotoluene (**24**). Anal. Calcd for $C_9H_9N_3O_5$: C, 45.20; H, 3.76; N, 17.56. Found: C, 45.01; H, 3.84; N, 17.39.

***N*-Methyl-2-amino-4,6-dinitrotoluene (25).** 2-Amino-4,6-dinitrotoluene (**10**)[10] (0.39 g, 2.0 mmol) was dissolved in 96% sulfuric acid (2 mL) at 130 °C, and paraformaldehyde (0.4 g) was added with stirring over 15 min. The mixture was heated at 130 °C for a further 45 min, cooled, and poured over ice. The precipitate was filtered off, washed and dried, and then extracted with dichloromethane (75 mL). The extract was dried over anhydrous magnesium sulfate and was evaporated to give an orange solid, which was recrystallized from dichloromethane/chloroform as orange crystals (0.405 g, 96%, mp 192–194 °C) (IR (KBr) 3430 (NH) and 1525 cm^{-1} (NO_2); NMR (acetonitrile-d_3) δ 7.96 (d, 1, Ar H, J = 3 Hz), 7.65 (d, 1, Ar H, J = 3 Hz), 3.13 (s, 3, NCH_3) and 2.23 (s, 3, $ArCH_3$)), identified as *N*-methyl-2-amino-4,6-dinitrotoluene (**25**). Anal. Calcd for $C_8H_9N_3O_4$: C, 45.45; H, 4.26; N, 19.91. Found C, 45.43; H, 4.29; N, 19.85.

Methylation of 3-amino-2,5-dinitrotoluene (**11**)[7] in the same manner afforded *N*-methyl-3-amino-2,5-dinitrotoluene (**26**) (75%, orange crystals from chloroform, mp 176.5–178 °C (IR (KBr) 3420 (NH) and 1530 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 7.43–7.75 (m, 2, Ar H), 3.13 (s, 3, NCH_3), and 2.60 (s, 3, $ArCH_3$)). Anal. Calcd for $C_8H_9N_3O_4$: C, 45.45; H, 4.26; N, 19.91. Found: C, 45.32; H, 4.30; N, 19.68.

Methylation of 4-amino-2,6-dinitrotoluene (**12**)[7] in the same manner gave *N*-methyl-4-amino-2,6-dinitrotoluene (**27**) (37%, orange crystals from chloroform, mp 137–139 °C) (IR (KBr) 3430 (NH) and 1535 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 7.15 (s, 2 Ar H), 3.15 (m, 1, NH), 2.90 (s, 3, NCH_3), and 2.40 (s, 3, $ArCH_3$)). Anal. Calcd for $C_8H_9N_3O_4$: C, 45.45; H, 4.26; N, 19.91. Found: C, 45.25; H, 4.40; N, 19.79.

***N*-Methyl-2-amino-*N*,3,4,5,6-pentanitrotoluene (28).** *N*-Methyl-2-amino-4,6-dinitrotoluene (**25**) (0.45 g, 2.1 mmol) was dissolved in 96% sulfuric acid (16 mL) and was cooled to 0 °C. Ninety percent nitric acid (1.35 mL) was added dropwise with stirring. The reaction mixture was stirred at 0 °C for 4 h and was then extracted with dichloromethane (5 × 50 mL). The extract was dried over anhydrous magnesium sulfate and evaporated to dryness. The residue was recrystallized from chloroform as pale yellow crystals (0.255 g, 35%, mp 173–175 °C) (IR (KBr) 1560 cm^{-1} (NO_2); NMR (acetonitrile-d_3) δ 3.70 (s, 3, NCH_3) and 2.48 (s, 3, $ArCH_3$)) identified as *N*-methyl-2-amino-*N*,3,4,5,6-pentanitrotoluene (**28**). Anal. Calcd for $C_8H_6N_6O_{10}$: C, 27.75; H, 1.74; N, 24.26. Found: C, 27.95; H, 1.83; N, 24.04.

Nitration of *N*-methyl-3-amino-2,5-dinitrotoluene (**26**) in the same manner afforded *N*-methyl-3-amino-*N*,2,4,5,6-pentanitrotoluene (**29**) (47%, pale yellow crystals from chloroform, mp 159–161 °C) (IR (KBr) 1550 cm^{-1} (NO_2); NMR ($CDCl_3$/acetone-d_6) δ 3.82 (s, 3, NCH_3) and 2.65 (s, 3, $ArCH_3$)). Anal. Calcd for $C_8H_6N_6O_{10}$: C, 27.75; H, 1.74; N, 24.26. Found: C, 27.65; H, 1.81; N, 24.10.

Nitration of *N*-methyl-4-amino-2,6-dinitrotoluene (**27**) in the same manner gave 4-amino-*N*,2,3,5,6-pentanitrotoluene (**17**) (21%), which was cleaved with anisole in 96% sulfuric acid to give 4-amino-2,3,5,6-tetranitrotoluene (**4**).

2-Amino-3,4,5,6-tetranitrotoluene (2). Method A. 2-Amino-4,6-dinitrotoluene (**10**) (3.0 g, 15.0 mmol) was dissolved in 96% sulfuric acid (150 mL) at ambient temperature. One hundred percent nitric acid (1.92 g, 60 mmol) was added dropwise with stirring, and the reaction mixture was stirred at ambient temperature for 24 h. The reaction mixture was extracted with dichloromethane (5 × 100 mL), and the extract was dried over anhydrous magnesium sulfate and was evaporated to give a yellow solid (0.95 g, 22%). Recrystallization from dichloromethane gave yellow crystals (0.60 g, mp 183–185 °C) (IR (KBr) 3450 and 3330 (NH) and 1550 cm^{-1} (NO_2); NMR (acetone-d_6) δ 8.20 (br s, 2, NH_2) and 2.4 (s, 3, $ArCH_3$)), identified as 2-amino-3,4,5,6-tetranitrotoluene (**2**). Anal. Calcd for $C_7H_5N_5O_8$: C, 29.36; H, 1.74; N, 24.38. Found: C, 29.25; H, 1.66; N, 24.14).

2-Amino-3,4,5,6-tetranitrotoluene (2). Method B. 2-Amino-4,6-dinitrotoluene (**10**) (1.0 g 5.0 mmol) was dissolved in 80% sulfuric acid (50 mL) at ambient temperature. Ninety percent (or 100%) nitric acid (3 mL) was added dropwise with stirring, and the reaction mixture was stirred at ambient temperature for 24 h. The yellow crystalline 2-amino-*N*,3,4,5,6-pentanitrotoluene (**17**) was filtered off and was air-dried. The solid was suspended in 96% sulfuric acid (50 mL), anisole (1 mL) was added, and the suspension was stirred at ambient temperature for 30 min. The reaction mixture was extracted with dichloromethane (5 × 75 mL); the extract was dried over anhydrous magnesium sulfate and was evaporated to leave a yellow solid (0.70 g, 48%). Recrystallization from dichloromethane gave 2-

amino-3,4,5,6-tetranitrotoluene (2) as yellow crystals (0.42 g, mp 183–185 °C).

Pentanitrotoluene (5). Method A. 2-Amino-3,4,5,6-tetranitrotoluene (2) (0.35 g, 1.1 mmol) was dissolved in 96% sulfuric acid (12.5 mL) and 30% oleum (10 mL). The solution was cooled to 0 °C, and 88% hydrogen peroxide (1.7 mL) was added dropwise with stirring. The solution was allowed to warm to ambient temperature and was stirred overnight. The reaction mixture was extracted with dichloromethane (4 × 50 mL); the extract was dried over anhydrous magnesium sulfate and was evaporated to give a pale yellow solid (0.30 g, 78%). Recrystallization from chloroform gave pale yellow crystals (0.24 g, mp 224–235 °C) (IR (KBr) 1550 cm^{-1} (NO_2); NMR (acetone-d_6) 2.71 (s, 3, CH_3)) identified as pentanitrotoluene (5). Anal. Calcd for $C_7H_3N_5O_{10}$: C, 26.50; H, 0.95; N, 22.08. Found: C, 26.64; H, 0.92; N, 21.97).

Dissolution of 3-amino-2,4,5,6-tetranitrotoluene (3) in a 1:2 mixture of 96% sulfuric acid and 20% oleum and oxidation using 98% hydrogen peroxide gave 5 in 79% yield, while oxidation of 4-amino-2,3,5,6-tetranitrotoluene (4) by the same method also yielded 5 in 82% yield.

3,5-Diamino-2,4,6-trinitrotoluene (30). Method A. Pentanitrotoluene (8) (0.20 g, 0.63 mmol) was dissolved in tetrahydrofuran (10 mL); a 0.4 N solution of ammonia in dioxane (30 mL) was added with an immediate color change from yellow to orange. After 10 min at ambient temperature, the solution was evaporated to dryness. Chromatography (silica gel/chloroform) gave a yellow solid, which was recrystallized from chloroform to give orange needles (0.12 g, 74%, mp 222.5–224 °C) (IR (KBr) 3440 and 3320 (NH_2) and 1600 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 8.30 (br s, 4, NH_2) and 2.40 (s, 3, $ArCH_3$)) identified as 3,5-diamino-2,4,6-trinitrotoluene (30).[15] Anal. Calcd for $C_7H_7N_5O_6$: C, 32.65; H, 2.73; N, 27.26. Found: C, 32.65; H, 2.71; N, 27.13.

3,5-Diamino-2,4,6-trinitrotoluene (30). Method B. 3-Amino-2,4,5,6-tetranitrotoluene (3) (0.109, 0.35 mmol) was dissolved in dioxane (5 mL); a 0.42 N solution of ammonia in dioxane was added with stirring. After 5 min, the reaction mixture was evaporated to dryness. The residue was dissolved in dichloromethane (25 mL) and was washed with water. Drying over anhydrous magnesium sulfate, evaporating, and recrystallization from chloroform/carbon tetrachloride gave orange crystals (0.06 g, 67%; mp 223–225 °C) identified as 3,5-diamino-2,4,6-trinitrotoluene (30).

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Alkoxyoxaziridines. Stereochemical Aspects of Imidate Oxidation, an Asymmetric Synthesis, and Unusually Facile *E–Z* Isomerizations[1]

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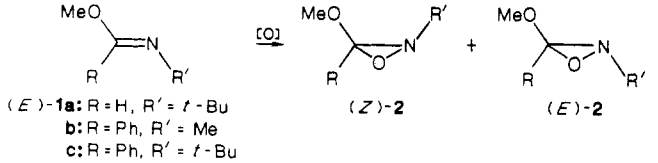
The synthesis of new, mechanistically useful 3-methoxy-3-phenyloxaziridines was accomplished by oxidation of imidate esters with *m*-chloroperbenzoic acid. Unlike previously known imidates, methyl *N-tert*-butylbenzimidate undergoes rapid *E–Z* isomerization at room temperature. Oxidation at ca. −10 °C gave 2-*tert*-butyl-3-methoxy-3-phenyloxaziridine [(*E*)-2c] in 22% yield as a 40:60 mixture of *E/Z* isomers in a kinetically controlled process. These and other stereochemical results suggest that oxidation occurs to some extent via a Baeyer–Villiger-type mechanism. Oxidation of methyl *N-tert*-butylformimidate with peroxycamphoric acid produced an excess of the *l* enantiomer of (*E*)-2-*tert*-butyl-3-methoxyoxaziridine. While most oxaziridines undergo slow N inversion, an unusually fast *E–Z* isomerization was observed for (*E*)-2c with activation parameters and an inverse solvent effect which suggested a zwitterion intermediate.

After the classic papers by Emmons,[2] investigations of oxaziridine chemistry entered a relatively dormant period,[3] but interest in this reactive ring system has recently been renewed with mechanistic,[4] reactivity,[5] and stereochemical studies.[6] In addition, two new classes of oxaziridines have been synthesized, one with a highly electron-withdrawing

Scheme I



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