

Synthesis of Tetranitrotoluenes

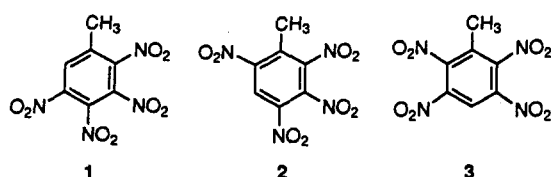
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New synthetic routes to the three isomeric tetranitrotoluenes 1-3 are described, including the previously unreported 2,3,4,5-tetranitrotoluene (1). Methods include peroxydisulfuric acid oxidation of trinitrotoluidines and hypophosphorous acid reduction of diazonium salts derived from tetranitrotoluidines. Synthesis of selected trinitrotoluidine precursors is also discussed.

Of the 19 possible nitrotoluenes (excluding those with nitro substitution at the methyl group), all had been prepared by 1920 except the tetranitrotoluenes (1-3) and pentanitrotoluene. The most important, the explosive



2,4,6-trinitrotoluene (α -TNT, TNT), was discovered by Wilbrand (1863).¹ Extensive studies of its synthesis and properties were reported by Beilstein and Kuhlberg as early as 1870.² Syntheses of the five remaining trinitrotoluene isomers were described in a group of articles published largely during the period 1914-1920.³

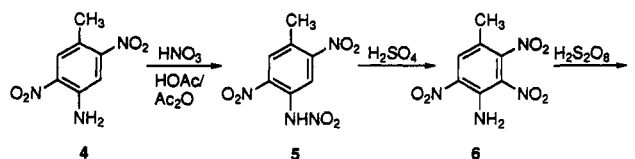
2,3,4,6-Tetranitrotoluene (2) was first reported by Borsche and Feske in 1926;⁴ a more efficient synthesis was reported by Holleman in 1930.⁵ More recently, publications from our laboratory described syntheses of 2,3,5,6-tetranitrotoluene (3) (but in modest yield at best)⁶ and pentanitrotoluene.⁷⁻¹⁰ We required the three isomers of tetranitrotoluene for investigation of the relationship of chemical structure with both density and explosive sensitivity. In this paper we describe two syntheses of the remaining unknown isomer 2,3,4,5-tetranitrotoluene (1), alternative and improved syntheses of 2 and 3, and syntheses of selected trinitrotoluidine precursors.

The synthesis of polynitrotoluenes is often accomplished conveniently and in high yield by oxidation of an appropriate polynitrotoluidine. Oxidizing agents such as

peroxy acids (peroxyacetic, peroxytrifluoroacetic) provide high yields of trinitrotoluenes.^{7,11} However, these particular oxidants are not sufficiently powerful for the conversion of trinitrotoluidines to tetranitrotoluenes. We have shown that peroxydisulfuric acid ($H_2S_2O_8$) oxidizes tri-, tetra-, and pentanitroanilines efficiently to previously unreported tetra-, penta-, and hexanitrobenzenes,⁷ as well as a tetranitrotoluidine to pentanitrotoluene.^{8,9} In the present work, this oxidant has been applied to the conversion of trinitrotoluidines into tetranitrotoluenes. Alternate methods of tetranitrotoluene synthesis are also presented and discussed.

Results and Discussion

Tetranitrotoluenes. Two synthetic procedures have been developed for the synthesis of the previously unreported 2,3,4,5-tetranitrotoluene (1). In the first, 4-amino-2,5-dinitrotoluene (4)¹² was nitrated with 90% HNO_3 in $HOAc/Ac_2O$ at 17-20 °C to yield nitramine 5. The Bamberger rearrangement of 5 to form the required 4-amino-2,3,5-trinitrotoluene (6) occurred in concd H_2SO_4 at 0 °C (88% yield from 5).⁶ Low reaction temperatures were required to maximize the yields in these reactions. Peroxydisulfuric acid oxidation of 6 gave 1 in 86% yield.



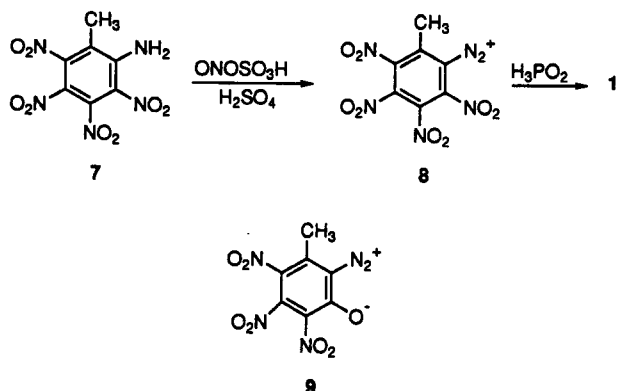
A second synthesis of 1 involves reduction of a diazonium salt intermediate. The tetranitrotoluidine precursor 7 is readily available from 2,4,6-trinitrotoluene (TNT).¹⁰ Reduction of TNT with iron and HOAc favors reduction of the 2-nitro group to yield 2-amino-4,6-dinitrotoluene.¹³ Nitration of the latter leads to 2-nitramino-3,4,5,6-tetranitrotoluene, which is denitrated to 7 by treatment with anisole in H_2SO_4 .¹⁰ Our initial attempts to diazotize 7 and reduce the intermediate diazonium salt 8 by known procedures were unsuccessful and led to mixtures containing diazo oxide impurity 9.⁶ (These compounds have also been referred to as diazophenols, but are probably better described as diazonium phenolates.) However, a procedure which employs a large excess of nitrosylsulfuric

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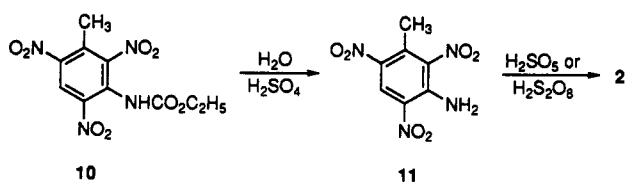
(11) (a) Emmons, W. D. *J. Am. Chem. Soc.* 1954, 76, 3470. (b) Emmons, W. D. *J. Am. Chem. Soc.* 1957, 79, 5528.
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acid in the diazotization step, followed by prolonged treatment with excess hypophosphorous acid, gave a 55% overall conversion of 7 to 1; reaction temperatures are held at 25 °C or below throughout.



2,3,4,6-Tetranitrotoluene (2) was first obtained by Borsche and Feske by oxidation of 3-(hydroxylamino)-2,4,6-trinitrotoluene with HNO_3 ; the yield was not reported.⁴ Holleman's more efficient procedure led to a 74% yield of 2 by heating 3-amino-2,4,6-trinitrotoluene (11) at 100 °C with Caro's acid (H_2SO_5 , from potassium persulfate and H_2SO_4). The toluidine 11 was obtained in 96% yield by reaction of 3-methoxy-2,4,6-trinitrotoluene with methanolic ammonia.^{5,14} Holleman also prepared 2 by reaction of the diazonium salt of 11 with nitrite ion, employing the procedure he had used for an efficient conversion of picramide into 1,2,3,5-tetranitrobenzene (69% yield); however, yields of 2 obtained by this method are very inferior.¹⁵

The synthetic scheme employed here was a modification of Holleman's oxidation route. Mixed acid nitration of the ethyl carbamate of *m*-toluidine gave the 2,4,6-trinitro derivative 10 in 88% yield. Hydrolysis of 10 occurred slowly in hot aqueous H_2SO_4 (90–95 °C, 6 h) to give an 88% yield of the trinitrotoluidine 11.^{16,17} Since peroxydisulfuric acid is such a powerful reagent for oxidation of polynitroanilines to polynitroaromatics (Caro's acid was not sufficiently powerful to oxidize picramide to 1,2,3,5-tetranitrobenzene, but peroxydisulfuric acid achieved the conversion in 93% yield⁷), that method was employed at 25 °C to convert 11 into pure 2,3,4,6-tetranitrotoluene (2) in 82% yield.⁷



The first synthesis of 2,3,5,6-tetranitrotoluene (3) was recently reported from our laboratory.⁶ It resulted during a study of polynitroaniline nitramines and their conversion into related diazo oxides. Heating nitramine 13 in refluxing acetone or ethyl acetate for 60 h gave a mixture of products, including 3 (isolated in 34% yield by column chromatography). Yields of 3 obtained from 13 by this method have been found to be variable, and modest at best.

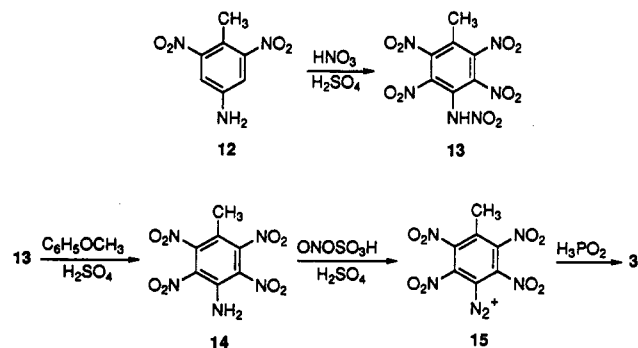
Table 1. Properties of Selected Polynitrotoluenes

compound	density, g/mL ^a	mp, °C ^b	¹ H NMR shifts: singlets, ppm ^c	
			aryl CH	CH ₃
2,4,6-trinitrotoluene (α -TNT)	1.65	80.5–81	8.81	2.69
2,3,4,5-tetranitrotoluene (1)	1.70	107–109	8.28	2.63
2,3,4,6-tetranitrotoluene (2)	1.69	135–136.5	8.74	2.64
2,3,5,6-tetranitrotoluene (3)	1.66	163–165	8.93	2.41
pentanitrotoluene	1.76	225–240 ^d	–	2.57

^a Gas pycnometer values, present work. ^b Recrystallized, analytically pure samples. ^c CDCl_3 solvent; tetramethylsilane internal reference; 30 °C. ^d Decomposition temperature range.

Heating 13 in dichloromethane under reflux for 4 days produced no reaction; heating in chloroform under reflux for 60 h produced the parent tetranitrotoluidine 14 (72% yield). In parallel experiments, 4-chloro-*N*,2,3,5,6-pentanitroaniline behaved differently when heated under reflux in acetone or ethyl acetate; it was recovered unchanged or produced 4-chloro-2,3,5,6-tetranitroaniline.⁶

In this study, 2,3,5,6-tetranitrotoluene (3) was prepared by reduction of 15, the diazonium salt of 4-amino-2,3,5,6-tetranitrotoluene (14), with hypophosphorous acid. The preparation of 15 proceeds from 4-amino-2,6-dinitrotoluene (12), obtained by reduction of α -TNT with H_2S and HI, which favors reduction of the 4-nitro group.¹⁸ Nitration of 12 occurs in $\text{HNO}_3/\text{H}_2\text{SO}_4$ at 0 °C to produce nitramine 13; denitration of 13 by treatment with anisole in H_2SO_4 gives 4-amino-2,3,5,6-tetranitrotoluene 14 (84% overall yield from 12). Reaction of 14 with nitrosylsulfuric acid in H_2SO_4 produces the diazonium salt 15, which when treated with hypophosphorous acid *in situ*, gives 3 in 65% overall yield from 14.



Some physical properties of the three isomeric tetranitrotoluenes, α -TNT, and pentanitrotoluene are summarized in Table 1. Melting points and densities increase with an increase in the number of nitro groups, although the tetranitrotoluenes are only slightly more dense than α -TNT. The tetra- and pentanitrotoluenes are thermally stable, and, like α -TNT, may be stored indefinitely at ambient temperature under anhydrous conditions.

Trinitrotoluidines. The isomeric trinitrotoluidines were seen as logical precursors for oxidation to the tetranitrotoluenes 1–3. However, only one of the ten possible trinitrotoluidines had been prepared previously, namely 3-amino-2,4,6-trinitrotoluene (11), precursor for tetranitrotoluene 2. (Numerous different syntheses of 11 have been reported, including ammonolysis of 3-chloro-, 3-bromo-, 3-methoxy- and 3-ethoxy-2,4,6-trinitrotoluene.^{5,14,19} We found convenient the hydrolysis of the

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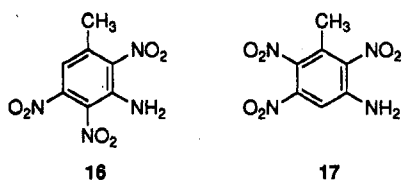
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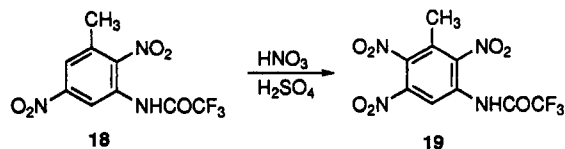
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carbamate 10, which has been described briefly elsewhere,^{16,17} and a detailed procedure is given in the Experimental Section.) Although we have prepared each of the 16 possible dinitrotoluidines¹⁸ and the 3 possible tetranitrotoluidines,¹⁰ synthesis of new trinitrotoluidines was found to be surprisingly difficult. (Ammonolysis of the tetranitrotoluidines 1-3 would presumably result in displacement of a nitro group, in the same manner as other polynitroaromatics,^{10,18,20} leading to various trinitrotoluidine isomers. This approach was clearly inappropriate for our purposes.) Most isomers were recognized as being possible but impractical precursors. However oxidation of 4-amino-2,3,5-trinitrotoluene (6) provided the favored route to 1, while 16 and 17 seemed suitable precursors for 1 and 3, respectively.



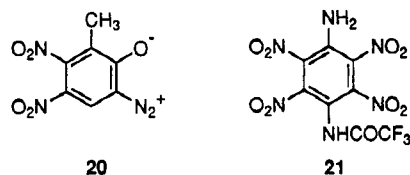
Direct nitration of certain dinitrotoluidines under rather mild conditions (HNO_3 , H_2SO_4 , HOAc ; 0 or 25 °C) has been reported to yield mixtures believed to contain *N*-nitro derivatives of three unknown trinitrotoluidines: 2-amino-3,4,6-trinitrotoluene, 4-amino-2,3,6-trinitrotoluene, and 3-amino-2,4,5-trinitrotoluene (16).^{6,10} The products were obtained as red or yellow oils, and usually contained diazo oxide impurities; none was purified or converted into the parent trinitrotoluidine. (The treatment of these nitramines with anisole in H_2SO_4 might be expected to produce trinitrotoluidines in a manner similar to the generation of the tetranitrotoluidines,¹⁰ but this reaction has not been investigated.)

Nitration of 3-amino-2,5-dinitrotoluene in $\text{HOAc}/\text{Ac}_2\text{O}$, followed by treatment of the crude product with concd H_2SO_4 , conditions used successfully for the sequence 4 \rightarrow 5 \rightarrow 6, failed to give either 16 or 17. By contrast, nitration of the trifluoroacetamide of 3-amino-2,5-dinitrotoluene (18) (HNO_3 , H_2SO_4 , 50–60 °C) occurred solely in the 6-position to yield 3-(trifluoroacetamido)-2,5,6-trinitrotoluene (19, 84% yield) (the trifluoroacetamide of 17). The structure assignment of 19 is based on the ¹³C-NMR chemical shifts of the CH_3 and C-1 aryl carbons. None of the isomeric trifluoroacetamide of 16 was detected.



Attempts to hydrolyze 19 to the parent amine 17 were unsuccessful. Heating 19 with methanolic HCl removed the trifluoroacetyl group to produce a diazo oxide, possibly 20. A variety of milder reaction conditions led to high recovery of 19; more vigorous conditions produced no identifiable crystalline products. Similar behavior was

exhibited by the related 2,3,5,6-tetranitro-4-(trifluoroacetamido)aniline (21). Numerous attempts to solvolyze 21



to 1,4-diamino-2,3,5,6-tetranitrobenzene were unsuccessful; recovered reactant and/or diazo oxides were obtained with aqueous H_2SO_4 . With most trinitro- and tetranitroanilines and their amides containing a nitro group in the 3 and/or 5 position) to nucleophilic displacement or rearrangement, formation of diazo oxides is favored under hot acidic conditions.^{6,18,21} However, 3-(trifluoroacetamido)- and 3-acetamido-2,4,6-trinitrotoluenes (in which the nitro groups are not thus activated) are more stable and may be hydrolyzed to the parent amine 11 in 95% yields by heating for 6 h in 80% H_2SO_4 at 90 °C.²²

Since the amide 19 could not be hydrolyzed to the parent amine 17, attempts were made to oxidize it directly to 3 using peroxydisulfuric and peroxytrifluoromethanesulfonic acids. These efforts were also unsuccessful, and 19 was recovered unchanged. There is precedent for the synthesis of tetranitroaromatics by peroxydisulfuric acid oxidation of certain trinitroacetanilides (but not trifluoroacetyl compounds).⁷ The *N*-acetyl and *N*-formyl equivalents of 18 were prepared, but, like the parent toluidine, these compounds decomposed on attempted nitration. This result may be compared with the attempted nitration of 2-acetamido-4,6-dinitrotoluene using mixed acid at 70 °C, where starting material was recovered unchanged.¹⁰

Experimental Section

Caution. The polynitro compounds described herein are powerful explosives and should be handled carefully. Diazo oxides are impact and friction-sensitive, hazardous materials.

Recovery of polynitroaromatics on recrystallization is frequently inefficient, and spectroscopically pure but unrecrystallized intermediates were therefore used for subsequent reactions. Infrared (IR) spectra were determined on a Perkin-Elmer Model 1330 infrared spectrophotometer. Nuclear magnetic resonance (NMR) spectra were determined on an IBM NR80 spectrometer. Melting points were determined on a Kofler hot stage and are uncorrected. Several compounds showed rather broad decomposition ranges, which are not uncommon with highly nitrated aromatics, and polynitroanilines in particular.^{7,8,10} Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

4-Amino-*N*,2,5-trinitrotoluene (5). To a solution of 4-amino-2,5-dinitrotoluene (4,¹² 1.50 g, 7.6 mmol) in acetic acid (100 mL), cooled to 17 °C, were added sequentially 90% HNO_3 (4.20 g, 60 mmol) and acetic anhydride (4.20 g, 40 mmol). The mixture was stirred at 17–20 °C for 0.5 h and then poured over ice-water (800 mL). The mixture, which contained a small amount of solid, was extracted with benzene (2 \times 1 L). The combined extracts, dried over MgSO_4 , were concentrated to dryness in high vacuum to afford 1.63 g (88%) of crude 5, mp 75–88 °C dec. Two recrystallizations, by dissolution in benzene at 25 °C and addition of hexane while scratching with a spatula, gave 5 (68% recovery), mp 82–90 °C dec; ¹H NMR (CDCl_3) δ 8.67 (s, 1 H, ArH), 8.23 (s, 1H, Ar H), 2.65 (s, 3H, CH_3); IR (KBr) cm^{-1} 3340 (NH), 3085 (CH), 1545 (NO_2). Anal. Calcd for $\text{C}_7\text{H}_6\text{N}_4\text{O}_6$: C, 34.72; H, 2.50;

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(22) Unpublished results, these laboratories.

N, 23.14. Found: C, 35.04; H, 2.37; N, 22.25. The low value for N is typical of primary aromatic nitramines, being a reflection of their poor stability. Support for the structure of 5 is derived from its conversion to 6 below.

4-Amino-2,3,5-trinitrotoluene (6). 4-Amino-*N*,2,5-trinitrotoluene (5, 0.50 g, 2.06 mmol) was stirred with concd H₂SO₄ (10 mL) at 0 °C for 69 h. The resulting solution was poured into ice-water (100 mL); the precipitate which formed was filtered off and washed with water to yield 0.44 g (88%) of crude 6, mp 145–151 °C. One recrystallization from hot ethanol gave pure 6 (40% recovery): mp 150–153 °C; ¹H NMR (CDCl₃) δ 8.42 (s, 1H, ArH), 7.92 (br s, 2H, NH₂), 2.29 (s, 3H, CH₃); IR (KBr) cm⁻¹ 3400 (NH₂), 1530 (NO₂). Anal. Calcd for C₇H₆N₄O₆: C, 34.72; H, 2.50; N, 23.14. Found: C, 35.03; H, 2.41; N, 22.70.

In parallel experiments, 3-amino-2,5-dinitrotoluene¹⁸ (0.25 g) nitration with 90% nitric acid in acetic acid/acetic anhydride produced reddish brown oils (0.20–0.26 g), which when stirred in concd H₂SO₄ at 25 °C, gave 0.25–0.29 g of oily solid from which only 3-amino-2,5-dinitrotoluene (15–20% recovery) could be isolated as a crystalline product; ¹H NMR spectra of the crude product indicate a mixture of ring-decomposition products, but no new nitrated toluidine.

2,3,4,5-Tetranitrotoluene (1) (Method A). To a solution of 4-amino-2,3,5-trinitrotoluene (6, 1.98 g, 8.17 mmol) in 100% H₂SO₄ (50 mL), protected by a CaCl₂ drying tube and cooled to 0 °C, was slowly added 90% H₂O₂ (10 mL) with stirring, keeping the temperature below 30 °C. After standing at 0 °C for 5 h, a second 10-mL portion of 90% H₂O₂ was added (< 30 °C) and stirring continued at 25 °C for 72 h. The mixture was extracted with CH₂Cl₂ (3 × 75 mL), and the combined extracts were dried with MgSO₄. Concentration of the extracts to dryness gave 1.92 g (86%) of crude 1, mp 95–102 °C. A single recrystallization from CHCl₃ gave pure 1 (93% recovery), mp 107–109 °C. Anal. Calcd for C₇H₄N₄O₈: C, 30.89; H, 1.48; N, 20.59. Found: C, 30.77; H, 1.54; N, 20.36.

2,3,4,5-Tetranitrotoluene (1) (Method B). Nitrosylsulfuric acid (0.25 g, 2.2 mmol) was added to a stirred solution of 2-amino-3,4,5,6-tetranitrotoluene (7, 10 mg, 0.17 mmol) in concd H₂SO₄ (3.0 mL) maintained at 2 °C. After stirring at 25 °C for 24 h, the solution was cooled to 2 °C and 0.25 g of additional nitrosylsulfuric acid was added, followed by stirring at 25 °C for 24 h. After cooling to 4 °C, H₃PO₂ (0.23 g of 50% aqueous solution, 1.8 mmol) was added (< 25 °C). After stirring at 25 °C for 4 h, another 0.23 g of 50% H₃PO₂ was added and the mixture stirred at 25 °C for 24 h. A third 0.23-g portion of 50% H₃PO₂ was added and the mixture stirred at 25 °C for 5 h. The mixture was then extracted with CH₂Cl₂ (3 × 5 mL), and the combined extracts dried with MgSO₄ and concentrated to dryness to yield 26 mg (55%) of crude 1, mp 65–78 °C; recrystallization from CHCl₃ gave crystalline 1, mp 107–109 °C, having NMR and IR spectra identical with a sample of 1 prepared by method A. In parallel runs employing only a single 0.23-g portion of 50% H₃PO₂, the product isolated was a mixture containing some diazo oxide 9, as evidenced by a strong band in the infrared spectrum at 2170 cm⁻¹.⁵

Ethyl *N*-(3-Methyl-2,4,6-trinitrophenyl)carbamate (10). The preparations of 10 and trinitrotoluidine 11 described below are improved and more detailed procedures than those previously reported.^{16,17} A solution of ethyl chloroformate (36 g, 0.33 mol) in dry benzene (50 mL) was slowly added, with stirring, to a mixture of *m*-toluidine (35 g, 0.327 mol) and Na₂CO₃ (15 g) in dry benzene (200 mL), keeping the temperature below 32 °C. After stirring for 1 h at 25 °C, the mixture was heated under reflux for 1 h, cooled to 30 °C, and filtered to remove a precipitate of salts which was washed with dry benzene. Distillation of the filtrate gave 51.5 g (88%) of ethyl *N*-(3-methylphenyl)carbamate, bp 106–110 °C (0.2 mm); lit.¹⁶ bp 103 °C (0.16 mm), 40% yield.

Ethyl *N*-(3-methylphenyl)carbamate (17.82 g, 0.10 mol) was added during 1 h, with stirring, to 100% HNO₃ (37.8 g, 0.60 mol) (< 25 °C). After stirring at 25 °C for 0.5 h, concd H₂SO₄ (50 mL) was added dropwise (< 30 °C), and stirring was continued at 25–40 °C for 2 h. The solution was poured into ice-water (1 L) and the mixture filtered to yield 27.8 g (88%) of crude 10, mp 105–150 °C; two recrystallizations from ethanol gave analytically pure 10 (60% recovery), mp 151–153 °C; ¹H NMR (CDCl₃) δ 0.30 (t, *J* = 7.1 Hz, 3H, CH₂CH₃), 2.58 (s, 3H, ring CH₃), 4.24 (q, *J* = 7.1

Hz, 2 H, CH₂CH₃), 8.73 (s, 1 H, aryl H) (lit.¹⁷ mp 153–154 °C after four recrystallizations). Anal. Calcd for C₁₀H₁₀N₄O₆: C, 38.22; H, 3.21; N, 17.83. Found: C, 38.16; H, 3.26; N, 17.67.

3-Amino-2,4,6-trinitrotoluene (11). A mixture of ethyl *N*-(3-methyl-2,4,6-trinitrophenyl)carbamate (10) (5.0 g, 16.0 mmol) and 80% H₂SO₄ (400 mL) was stirred and heated at 90–95 °C for 6 h. After cooling to 25 °C, the mixture was poured onto ice (600 g) and the resulting precipitate filtered and washed with water to yield 3.39 g (88%) of crude 11, mp 115–134 °C; one recrystallization from ethanol gave 11 as prisms (50% recovery), mp 135–136 °C, having an ¹H NMR spectrum identical with an authentic sample: δ (CDCl₃) 2.60 (s, 3H, CH₃), 9.06 (s 1 H, aryl H); lit. mp 136 °C,^{19b,c} 137 °C,¹⁷ 138 °C,¹⁴ 138–138.5 °C.¹⁶ (In parallel experiments 3-acetamido- and 3-trifluoroacetamido-2,4,6-trinitrotoluenes (both prepared from 11) were each completely hydrolyzed to 11 in 6 h in 95% yield.²²)

4-Amino-2,3,5,6-tetranitrotoluene (14). The following are modified, improved procedures leading to 13 and 14.¹⁰ To a solution of 4-amino-2,6-dinitrotoluene (12,¹⁶ 4.34 g, 22 mmol) in concd H₂SO₄ (175 mL) at 5 °C was slowly added 90% HNO₃ (13 mL) with stirring, keeping the temperature below 25 °C. After stirring at 25 °C for 3 h, the solution was extracted with CH₂Cl₂ (3 × 250 mL), and the combined extracts were dried with MgSO₄ and concentrated to dryness to yield 5.78 g (79%) of crude 4-amino-*N*,2,3,5,6-pentanitrotoluene (13), mp 137–167 °C. To the crude 13 (5.78 g), dissolved in concd H₂SO₄ (600 mL) (< 10 °C), was added anisole (2.1 g) with stirring (< 5 °C), followed by stirring at 0–5 °C for 45 min. The mixture was immediately poured over ice (2.5 kg), and the precipitate filtered and washed with water to yield 5.30 g (84% from 12) of crude 14, mp 170–235 °C; recrystallization from CH₂Cl₂ gave 14 as platelets (75% recovery), which changed to needles near the melting point, 225–242 °C (lit.¹⁰ mp 230–235 °C); ¹H NMR (CDCl₃) δ 2.22 (s, CH₃).

2,3,5,6-Tetranitrotoluene (3). A solution of 4-amino-2,3,5,6-tetranitrotoluene (14, 100 mg, 0.35 mmol) in concd H₂SO₄ (4 mL) cooled to 2 °C was treated with nitrosylsulfuric acid (0.5 g, 4.4 mmol). After stirring at 25 °C for 16 h and cooling to 2 °C, 0.5 g of additional nitrosylsulfuric acid was added and the mixture stirred at 25 °C for 8 h. After cooling to 2 °C, 50% H₃PO₂ (0.92 g, 7.2 mmol) was added dropwise (< 25 °C); stirring was continued at 25 °C for 16 h, followed by addition of more 50% H₃PO₂ (0.46 g). The mixture was then stirred and heated at 50 °C for 1 h and at 25 °C for 3 h. It was then extracted with CH₂Cl₂ (3 × 5 mL), and the extracts were dried with MgSO₄ and concentrated to dryness to yield 64 mg (68%) of crude 3, mp 141–163 °C. Two recrystallizations from CHCl₃ gave pure 3 as rectangular platelets (80% recovery): mp 163–165 °C, lit.⁵ mp 150–152 °C. Anal. Calcd for C₇H₄N₄O₈: C, 30.89; H, 1.48; N, 20.59. Found: C, 30.76; H, 1.55; N, 20.28.

2,5-Dinitro-3-(trifluoroacetamido)toluene (18). A mixture of 3-amino-2,5-dinitrotoluene¹⁸ (0.50 g, 2.5 mmol) and trifluoroacetic anhydride (15 mL) was heated, with stirring, under reflux for 1 h. Concentration of the mixture to dryness gave 0.70 g (94%) of crude 18, mp 126–130 °C. Recrystallization from aqueous ethanol gave pure 18 (67% recovery): mp 129–130 °C; ¹H NMR (CDCl₃) δ 2.70 (s, 3H, CH₃), 8.20 (s, 1H, ArH), 9.12 (s, 1H, ArH), 9.40 (br s, 1H, NH); IR (KBr) 1750 cm⁻¹, C=O. Anal. Calcd for C₉H₆F₃N₃O₆: C, 36.87; H, 2.07; F, 19.44; N, 14.34. Found: C, 36.91; H, 2.26; F, 19.24; N, 14.03.

3-(Trifluoroacetamido)-2,5,6-trinitrotoluene (19). A mixture of 2,5-dinitro-3-(trifluoroacetamido)toluene (18, 2.0 g, 6.8 mmol), concd H₂SO₄ (5.0 g), and 90% HNO₃ (5.6 g) was stirred and heated at 50–60 °C for 2 h. After cooling to 25 °C, the mixture was poured into ice water (175 mL) and filtered, and the precipitate was washed with water to yield 1.93 g (84%) of 19, mp 138–143 °C; recrystallization from hot ethanol gave crystals, mp 135–141 °C; IR (KBr) 1700 cm⁻¹, C=O. Anal. Calcd for C₉H₅F₃N₃O₇: C, 31.96; H, 1.49; F, 16.86; N, 16.57. Found: C, 31.86; H, 1.76; F, 16.57; N, 16.17. ¹H NMR (CDCl₃) δ 2.53 (s, 3H, CH₃), 9.20 (s, 1 H, ArH); ¹³C NMR (CDCl₃) δ 14.2 (CH₃), 129.1 (aryl C-1). For reference: 2,3,6-trinitrotoluene ¹³C NMR (CDCl₃) δ 14.2 (CH₃), 128.6 (aryl C-1) and 2,4,5-trinitrotoluene δ 20.7 (CH₃), 142.3 (aryl C-1).

Attempted oxidation of 19 with 98% H₂O₂/100% H₂SO₄ or trifluoromethanesulfonic acid at 25 °C gave recovered 19. Reaction of 19 (100 mg) with excess methanolic HCl at 60 °C for

15 min gave 75 mg of reddish-brown solid: mp 141–154 °C; IR (KBr) strong diazo oxide band at 2120 cm^{-1} ; C=O band absent; the material was not investigated further. Attempted reaction of 19 with 50% aqueous H_2SO_4 at 50 °C for 2 h gave recovered 19.

3,5-Dinitro-4-(trifluoroacetamido)aniline. A solution containing HNO_3 (90%, 40 mL, 0.9 mol) and 22% oleum (20 mL) was added to a solution of 4-(trifluoroacetamido)benzoic acid²³ (11.65 g, 50 mmol) in 22% oleum (60 mL) (<30 °C). After heating, with stirring at 45 °C for 1.5 h, followed by cooling to 10 °C, the mixture was filtered and washed with 50% H_2SO_4 and then water to yield 13.3 g (82%) of 3,5-dinitro-4-(trifluoroacetamido)benzoic acid, mp 260 °C.

Sodium azide (3.9 g, 60 mmol) was added slowly, with stirring, to a solution of 3,5-dinitro-4-(trifluoroacetamido)benzoic acid (12.9 g, 40 mmol) in 22% oleum (75 mL) under a blanket of 1,2-dichloroethane (60 mL) (<25 °C). After heating and stirring at 80 °C for 2 h,⁷ the mixture was cooled to 25 °C and poured into ice (1.7 L), filtered, and washed with water to yield 8.46 g of product; an additional 1.07 g of product was obtained by adjusting the pH of the filtrate to 2.5 by addition of sodium acetate (250 g); total yield of crude product 9.53 g (81%), mp 183–185 °C. Recrystallization from 1,2-dichloroethane gave pure 3,5-dinitro-4-(trifluoroacetamido)aniline (54% recovery), mp 183.5–185.5 °C; IR (KBr) 1680 cm^{-1} (C=O); ^1H NMR (CD_3CN) δ 7.62 (s); ^{19}F NMR (CD_3CN , 94.1 MHz ref to $\text{CFCl}_3 = 0.00$) δ 30.85. Anal. Calcd for $\text{C}_8\text{H}_6\text{F}_3\text{N}_4\text{O}_6$: C, 32.67; H, 1.71; F, 19.38; N, 19.05. Found: C, 32.50; H, 1.74; F, 19.19; N, 18.84.

2,3,5,6-Tetranitro-4-(trifluoroacetamido)aniline (21). A solution of 90% HNO_3 (18 mL, 360 mmol) in concd H_2SO_4 (75 mL) was added dropwise over 7 min to a solution of 3,5-dinitro-4-(trifluoroacetamido)aniline (8.46 g, 28.8 mmol) in concd H_2SO_4 (250 mL) at 0 °C, and the mixture was stirred at ambient temperature for three h. The orange solid was filtered off, washed with cold 50% aqueous H_2SO_4 and then cold water, and finally dried under vacuum at ambient temperature to yield 6.47 g (52%) of crude *N*,2,3,5,6-pentanitro-4-(trifluoroacetamido)aniline: mp 109–110 °C dec; IR (KBr) 3220 (br, s) 1730 (s), 1550 (br, vs) cm^{-1} . Anisole (6.5 mL, 60 mmol) was added to a mixture of *N*,2,3,5,6-pentanitro-4-(trifluoroacetamido)aniline (6.32 g, 14.7 mmol) and concd H_2SO_4 (500 mL). After stirring at 25 °C for 1.5 h, the mixture was extracted with CH_2Cl_2 (10 \times 300 mL); the combined extracts were dried with MgSO_4 and evaporated to dryness to yield 3.84 g (68%) of crude 21, mp 167–169 °C dec. Recrystallization from 1,2-dichloroethane gave 21 as orange crystals (87% recovery): mp 173–174 °C; IR (KBr) 1740 cm^{-1} (C=O); ^{19}F NMR (CD_3CN , 94.1 MHz, ref to $\text{CFCl}_3 = 0.00$) δ 31.40. Anal. Calcd for $\text{C}_8\text{H}_3\text{F}_3\text{N}_8\text{O}_9$: C, 25.01; H, 0.79; F, 14.84; N, 21.88. Found: C, 25.06; H, 0.87; F, 14.79; N, 21.69.

Attempted hydrolysis of 21 to 1,4-diamino-2,3,5,6-tetranitrobenzene in numerous separate experiments with 50–80%

H_2SO_4 or other acids ($\text{CF}_3\text{CO}_2\text{H}$, $\text{CF}_3\text{SO}_3\text{H}$, $\text{CH}_3\text{CO}_2\text{H}$) at 25–85 °C gave recovered 21 and/or unidentified diazo oxide(s) (IR band at 2120 cm^{-1}) and no other crystalline products. Heating 21 (120 mg) in refluxing methanol (5 mL, without added acid catalyst) for 20 min, followed by concentration to dryness, gave a decomposition product (86 mg, 90%), mp 241–243 °C, believed to be 3-methoxy-2,5,6-trinitro-4-(trifluoroacetamido)aniline:²⁴ IR (KBr) 1710 cm^{-1} (C=O); ^1H NMR δ 4.08 (s, CH_3O). Anal. Calcd for $\text{C}_9\text{H}_6\text{F}_3\text{N}_5\text{O}_8$: C, 29.28; H, 1.64; F, 15.44; N, 18.97. Found: C, 29.42; H, 1.66; F, 15.46; N, 18.98.

3-Acetamido-2,5-dinitrotoluene. A mixture of 3-amino-2,5-dinitrotoluene¹⁸ (0.25 g, 1.27 mmol), acetic anhydride (3 mL), and a drop of concd H_2SO_4 was heated, with stirring, at 90–95 °C for 1 h. The excess acetic anhydride was removed under reduced pressure (50 °C). The residue was diluted with 5 mL each of water and methanol and stored at 0 °C; the resulting precipitate was filtered off and washed with water to yield 0.29 g (96%) of crude product, mp 106–126 °C. Recrystallization from methanol gave pure amide as needles (63% recovery): mp 133–135 °C; ^1H NMR (CDCl_3) δ 2.32 (s, 3H, CH_3CO), 2.51 (s, 3H, CH_3 ring), 7.98 (s, 1 H, ArH), 8.32 (br s, 1 H, NH), 9.12 (s, 1 H, ArH). Anal. Calcd for $\text{C}_9\text{H}_9\text{N}_3\text{O}_5$: C, 45.19; H, 3.79; N, 17.57. Found: C, 45.24; H, 3.80; N, 17.41.

Attempted preparation of a 3-acetamidotrinitrotoluene by nitration of this amide, using the procedure employed for preparation of the trifluoroacetamido derivative 19 from 18, led to gums from which no crystalline product could be isolated. In parallel experiments, attempted nitration of the amide at 30–40 °C led to recovered starting material.

3-Formamido-2,5-dinitrotoluene. 3-Amino-2,5-dinitrotoluene¹⁸ (5.0 g, 25.3 mmol) was added to a solution of acetic formic anhydride prepared by heating acetic anhydride (4.7 mL) and formic acid (1.88 mL) at 50–60 °C for 2 h.²⁵ After stirring the mixture at 25 °C for 64 h, the resulting precipitate was filtered and washed with acetic anhydride (5 mL) to yield 3.37 g (59%) of crude product, mp 141–147 °C; recrystallization from methanol gave rectangular prisms of pure formamide (50% recovery): mp 144–147 °C; ^1H NMR δ 2.55 (s, 3 H, CH_3), 7.99 (s, 1 H, CHO), 8.34 (s, 1 H, NH), 8.51 (s, 1 H, ArH), 9.15 (s, 1 H, ArH). Anal. Calcd for $\text{C}_8\text{H}_7\text{N}_3\text{O}_5$: C, 42.67; H, 3.13; N, 18.66. Found: C, 42.96; H, 3.49; N, 18.37.

Attempted preparation of a 3-formamidotrinitrotoluene by the procedure employed in the conversion of 18 to 19 led to gums from which no crystalline product could be isolated.

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