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# Synthesis of Polynitrobenzenes. Oxidation of Polynitroanilines and Their *N*-Hydroxy, *N*-Methoxy, and *N*-Acetyl Derivatives

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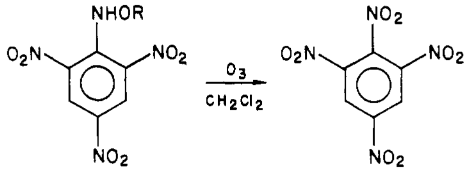
Nitro-substituted arylhydroxylamines and alkoxyamines have been oxidized to polynitroaryl compounds by utilizing ozone. Polynitroanilines have been oxidized to polynitroaromatics by peroxydisulfuric acid generated in situ from $SO_3$ and ozone. Thus *N*-hydroxy-2,4,6-trinitroaniline (**1a**) or *N*-methoxy-2,4,6-trinitroaniline (**1b**) was cleanly oxidized to 1,2,3,5-tetranitrobenzene (**2**) by reaction with ozone in methylene chloride. Weakly basic amines such as pentanitroaniline (**10**) can conveniently be oxidized to hexanitrobenzene (**11**) in high yields by simply dissolving the amine in oleum and introducing ozone. A variety of substituted arylamines have been oxidized to polynitroaromatic compounds by using these two oxidation techniques.

Nitro compounds are conveniently prepared by direct oxidation of the corresponding amine, using as oxidants peracids such as Caro's acid (peroxysulfuric acid),[3] peracetic acid,[4] peroxytrifluoroacetic acid,[5] permaleic acid,[6] *m*-chloroperbenzoic acid,[7] and perbenzoic acid.[8] However, these methods have proven inadequate for the oxidation of weakly basic amines such as aminopolynitroaromatics. A technique has recently been developed in these laboratories to achieve this oxidation, using peroxydisulfuric acid prepared in situ by the addition of 90–98% hydrogen peroxide to 100% sulfuric acid or oleum.[9a] This method has been used successfully for the synthesis of a large number of tri-, tetra-, penta-, and hexanitrobenzenes, -fluorobenzenes, and -toluenes, as well as several polynitropolyaromatics.[9b] However, hydrogen peroxide of this concentration is not always readily available and is a rather hazardous material, being a very powerful oxidant in its own right. In these laboratories the addition of concentrated hydrogen peroxide to oleum containing a fuel such as an aminopolynitroaromatic compound has occasionally led to "fume-offs" or runaway thermal reactions. Alternative oxidation methods were therefore considered desirable.

Attempts to oxidize aminopolynitroaromatics (such as picramide (2,4,6-trinitroaniline) or pentanitroaniline) in inert solvents with ozone have resulted in low yields accompanied with decomposition. Keinan and Mazur report some limited success in which the passage of ozone over various anilines supported on dry silica gel has given low yields of the corresponding nitrobenzenes.[10] Strecker and Baltes report the oxidation of phenylhydroxylamine to give nitrobenzene, but report no yield.[11] In our hands, the oxidation of phenylhydroxylamine with ozone in chloroform following the procedure of Strecker and Baltes gave a low yield of dark oil that contained some nitrobenzene (identified by gas chromatography). Similarly, Bachman and Strawn reported the oxidation of a number of amines and amine derivatives with ozone to give in low to poor yields the corresponding nitro derivatives.[12] They report a 16.4% yield of nitrobenzene from phenylhydroxylamine. They also did not isolate the product but identified it by gas chromatographic analysis. Borsche has reported the oxidation of 2,4- and 2,6-dinitrophenylhydroxylamines to the corresponding 1,2,4- and 1,2,3-trinitrobenzenes by heating the precursors in fuming nitric acid.[13] These conditions, while effective for these substrates, are far too harsh for many of the compounds of interest to us.

Scheme I



1a, R = H
b, R = Me

2

In the work reported here, oxidation of (hydroxyamino)- and (methoxyamino)polynitroaromatics in inert solvents by ozone has been more successful, and results of these experiments are summarized in Table I. Thus passage of ozone through a solution of *N*-hydroxy-2,4,6-trinitroaniline (**1a**) in methylene chloride at −10 °C gave 1,2,3,5-tetranitrobenzene (**2**) in essentially quantitative yield after only 15 min. The product was identical in all respects with an authentic sample prepared by peroxydisulfuric acid oxidation of picramide.[9b] *N*-Methoxy-2,4,6-trinitroaniline (**1b**) was oxidized in a similar fashion and in high yield to the same product. However, in this instance the oxidation was considerably slower, the reaction requiring 75 min for completion compared with 15 min for the hydroxylamine (Scheme I).

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[2] This work was carried out at the Naval Weapons Center during an exchange of scientists under the Technical Cooperation Program.

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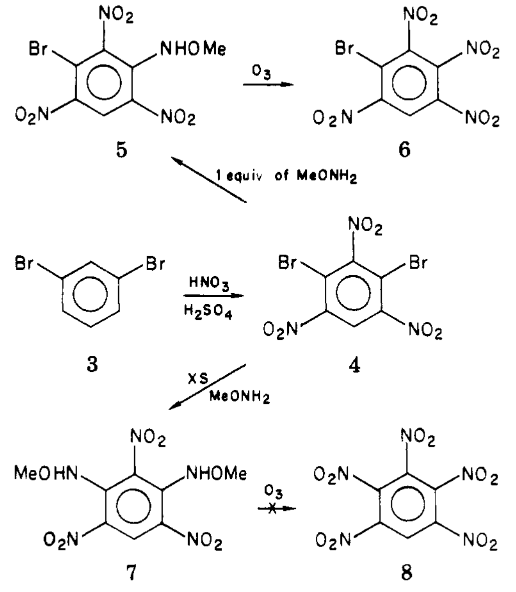
Table I. Ozone Oxidation of *N*-Hydroxy- and *N*-Methoxypolynitroanilines

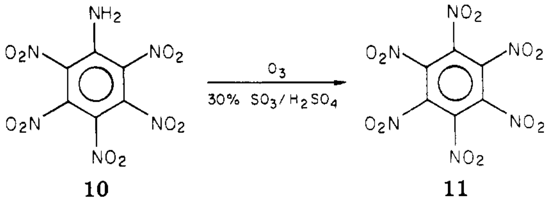
| no. | compound | solvent | temp, °C | rctn time, min | no. | product | yield,[a] % | mp,[b] °C |
|---|---|---|---|---|---|---|---|---|
| 1a | *N*-hydroxy-2,4,6-trinitroaniline | $CH_2Cl_2$ | −10 | 15 | 2 | 1,2,3,5-tetranitrobenzene | 100 | 124–125 |
| 1b | *N*-methoxy-2,4,6-trinitroaniline | $CH_2Cl_2$ | −10 | 75 | 2 | 1,2,3,5-tetranitrobenzene | 100 | 125–129 |
| 5 | *N*-methoxy-3-bromo-2,4,6-trinitroaniline | ethyl acetate | 25 | 120 | 6 | 2,3,4,6-tetranitro-1-bromobenzene | 100 | 113–114 |
| 7 | 1,3-bis(methoxyamino)-2,4,6-trinitrobenzene | ethyl acetate | 25 | 120 | *c* | *c* | *c* | *c* |
| 19 | *N*-methoxy-2,4-dinitro-2-methoxyaniline | $CH_2Cl_2$ | −35 | 25 | 20 | 1,2,6-trinitroanisole | 95 | 28–29 |
| 20 | *N*-hydroxy-3,5-dinitroaniline | $CH_2Cl_2$ | −35 | 25 | 22 | 1,3,5-trinitrobenzene | 100 | 121–122 |

[a] Isolated yields; significant losses occur on recrystallization, however, the product polynitrobenzenes show no impurities in their respective IR and NMR spectra. [b] Melting point of recrystallized sample. [c] No products were isolable.

Scheme II



Scheme III



Many hydroxyamino- and alkoxyamino-substituted aromatic compounds may be prepared easily by nucleophilic displacement of a variety of leaving groups by hydroxylamine and alkoxyamines. These displacement reactions may be carried out under very mild conditions compared with the usual conditions for mixed acid nitration; therefore, this new sequence offers a useful pathway for the insertion of nitro groups into aromatic ring systems. For example, 2,4-dibromo-1,3,5-trinitrobenzene (**4**) was obtained readily by routine mixed acid nitration of 1,3-dibromobenzene (**3**).[14] Treatment with a small excess of methoxyamine gave *N*-methoxy-3-bromo-2,4,6-trinitroaniline (**5**), while an excess of methoxyamine gave 2,4-bis(methoxyamino)-1,3,5-trinitrobenzene (**7**). The corresponding hydroxyamino and bis(hydroxyamino) derivatives could not be prepared from the reaction of hydroxylamine with **4** under a variety of reaction conditions.

The passage of ozone through a solution of **5** in ethyl acetate or carbon tetrachloride at ambient temperature gave essentially quantitative oxidation to 2,3,4,6-tetranitro-1-bromobenzene (**6**). On the other hand, treatment of **7** in a similar fashion gave no isolable pentanitrobenzene (**8**) but resulted in a complex mixture of products. Prolonged passage of ozone through a solution of **7** in carbon tetrachloride also gave a complex mixture of products. Mass spectral analysis indicated the presence of pentanitrochlorobenzene and a tetranitrodichlorobenzene (Scheme II). It seems that the presence of the two methoxyamino groups so retarded the oxidation reaction that solvent participation becomes a competitive process. It should be noted that neither *N*-hydroxy-2,3,4,6-tetranitroaniline (**9**) nor the *N*-methoxy compound could be isolated from the reaction of hydroxylamine or methoxyamine with 2,3,4,6-tetranitro-1-bromobenzene (**6**), and this alternative stepwise route to pentanitrobenzene was therefore unsuccessful. Attempts to introduce two nitro groups into the same aromatic nucleus by other oxidative methods have been similarly unsuccessful. It should also be stressed that the present study has been restricted to the oxidation of (hydroxyamino)- and (methoxyamino)-polynitroaromatics. However, it is anticipated that the reaction will be general for (alkoxyamino)polynitroaromatics.

Peroxydisulfuric acid has also been prepared by the action of gaseous ozone on oleum.[15] This suggested itself as an attractive alternative for the in situ generation of peroxydisulfuric acid for the oxidation of aminopolynitroaromatics, and indeed such proved to be the case. When ozone was bubbled through a stirred solution of an aminopolynitroaromatic precursor dissolved in oleum at ambient temperature for 2–3 days, extraction with methylene chloride and recrystallization from chloroform gave material identical in all respects with that obtained by using 90–98% hydrogen peroxide in oleum as oxidant.[9] The reaction conditions and results are summarized in Table II below.

The potential of the reaction was first examined by passing ozone through a solution of pentanitroaniline (**10**) in oleum at room temperature (Scheme III). Attempts to oxidize **10** with ozone in inert solvents ($CH_2Cl_2$, $CCl_4$) led to decomposition of the starting material, while ozonization in 100% sulfuric acid resulted in essentially quantitative recovery of **10**. A 45% conversion to hexanitrobenzene (**11**) was obtained after passing ozone through a solution of the amine in 30% oleum for 24 h. The yield could be increased to 78% by continuing the reaction for 48 h but decreased with longer reaction times.

Similarly, treatment of 4-amino-2,3,5,6-tetranitrotoluene (**12**) in 15% oleum (Scheme IV) at room temperature with

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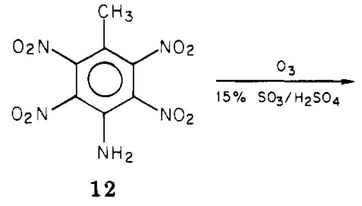
Table II. Ozone Oxidation of Amino- and Acetamidopolynitro Compounds in Oleum Solution. In Situ Generation of Peroxydisulfuric Acid

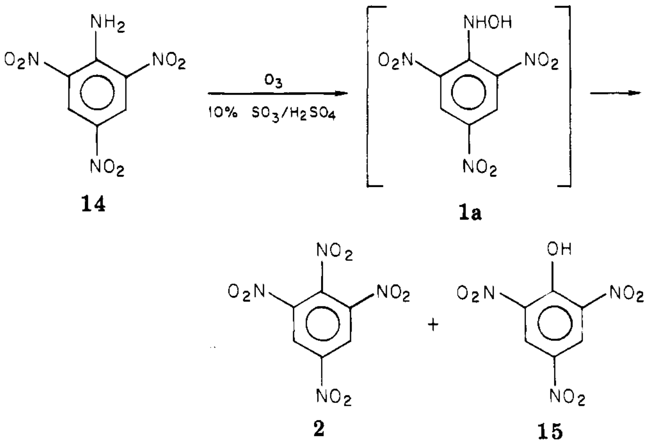
| no. | compound | acid strength (% $SO_3$) | rctn time, h | no. | product | yield,[a] % | mp,[b] °C |
|---|---|---|---|---|---|---|---|
| 10 | 2,3,4,5,6-pentanitroaniline | 30 | 48 | 11 | hexanitrobenzene | 78 | 245-260 |
| 12 | 4-methyl-2,3,5,6-tetranitroaniline | 15 | 48 | 13 | 2,3,4,5,6-pentanitrotoluene | 57 | 225-240 |
| 14 | 2, 4,6-trinitroaniline | 10 | 72 | 2 | 1,2,3,4-tetranitrobenzene | 49 | 125-129 |
| 16 | 2,4,6-trinitroacetaniline | 10 | 72 | 2 | 1,2,3,4-tetranitrobenzene | 29 | 125-129 |
| 17 | 1,3-diamino-2,4,6-trinitrobenzene | 0-30 | 72 | [c] |  | 100% dec |  |
| 18 | 1,3-diacetamido-2,4,6-trinitrobenzene | 0-30 | 72 | [c] |  | 100% dec |  |

[a] Isolated yields; significant losses occur on recrystallization, however, the product polynitrobenzenes show no impurities in their respective IR and NMR spectra. [b] Isolated yields; as is usually the case with polynitroaromatics, significant losses occur on recrystallization. [c] No products were isolable.

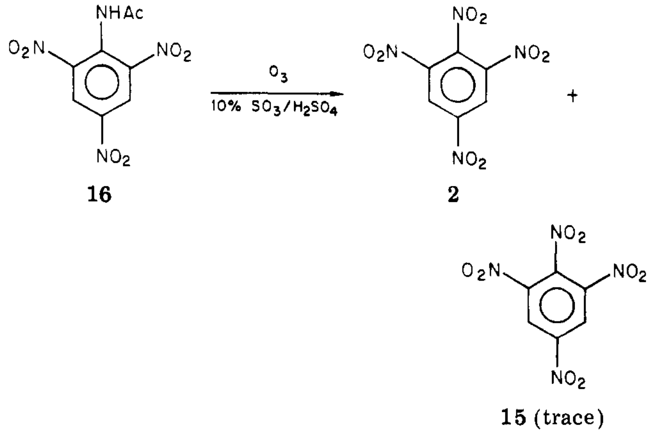
Scheme IV



Scheme V



Scheme VI



ozone for 48 h gave pentanitrotoluene (**13**) in 57% yield. There was no indication of oxidation of the methyl group. This may be compared with the ready oxidation of 2,4,6-trinitrotoluene to 2,4,6-trinitrobenzoic acid by potassium permanganate or sodium dichromate in concentrated sulfuric acid.

Treatment of picramide (**14**) (Scheme V) in 15–30% oleum with ozone for 24 h gave only about 5% of the expected 1,2,3,5-tetranitrobenzene (**2**). However, when the oxidation was carried out for 72 h in 10% oleum, the yield was improved to 49%. The product was contaminated with about 5% picramide and picric acid (**15**). While both picramide and tetranitrobenzene are stable with respect to hydrolysis under the conditions of reaction and workup, the presumed oxidation intermediate, *N*-hydroxy-2,4,6-trinitroaniline (**1a**), may undergo disproportionation to **14** and **15** under the reaction conditions. However, while this hydroxylamine is converted to picramide over a period of several days in 10% oleum, picric acid could not be detected. Further, as has been shown in this study, the hydroxylamine is very rapidly oxidized by ozone to 1,2,3,5-tetranitrobenzene (**2**). It is also interesting to note that the corresponding phenols were not detected following oxidation of either pentanitroaniline or 4-amino-2,3,5,6-tetranitrotoluene by this method.

The oxidation of aminopolynitroaromatics by peroxydisulfuric acid is frequently very vigorous, and this reactivity has sometimes been moderated by using *N*-acetyl derivatives in place of the parent amine.[9b] Therefore, it was of interest to determine whether these amides could be oxidized when the peroxydisulfuric acid was generated much more slowly by bubbling ozone into oleum. The passage of a stream of ozone through a solution of *N*-acetyl-2,4,6-trinitroaniline (**16**) (Scheme VI) in 10% oleum for 72 h under ambient conditions gave 1,2,3,5-tetranitrobenzene (**2**) in 29% yield, again with a trace of picric acid being formed.

Since the oxidation of aminopolynitroaromatics with peroxydisulfuric acid generated by the passage of ozone is much slower than when the oxidant is generated by the addition of 90–98% hydrogen peroxide, it was thought that such compounds as 1,3-diamino-2,4,6-trinitrobenszene (**17**), which contain two amine functional groups on the same aromatic nucleus and which "fume off" under the oxidation conditions developed earlier,[9] might be oxidizable by using the method reported here. However, at a variety of acid strengths from 96% sulfuric acid to 30% oleum both **17** and its diacetyl derivative **18** were smoothly but completely fragmented when treated with ozone gas in oleum, and no organic produce was isolable from the reaction mixture. The presence of two electron-releasing substituents on the aromatic ring leads to activation of the aromatic ring to oxidation and results in destructive oxidation of the aromatic nucleous.

In summary, two methods have been developed for the introduction of nitro groups into polynitroaromatics. The first is a high yield oxidation with ozone of (hydroxyamino)- and (methoxyamino)polynitroaromatics, prepared by nucleophilic substitution under mild conditions. In the second method, aminopolynitroaromatics and their *N*-acetyl derivatives are oxidized by peroxydisulfuric acid generated in situ by bubbling ozone into a solution of the amine or amide in oleum. This provides a useful alternative to the addition of 90–98% hydrogen peroxide to a solution of the amine in oleum, although the reactions are somewhat slower and the yields lower. However, the simultaneous introduction of two nitro groups into the same aromatic nucleus by either of these methods has proven difficult, as indeed it has using other methods.

## Experimental Section

**Warning!** Polynitroaromatics are powerful explosives and should be handled with great care. Satisfactory elemental analyses were obtained for all new compounds; all previously known compounds were spectrally identical with authentic materials prepared by established procedures. Melting points were determined in capillary tubes with a Büchi 510 melting point apparatus. Infrared spectra were recorded as potassium bromide disks with a Perkin-Elmer 137 spectrophotometer. Proton magnetic resonance spectra were recorded with a Varian 360 NMR spectrometer, using tetramethylsilane as an internal standard. A Welsbach ozone generator was employed, giving a 3–4% solution of ozone in oxygen.

**Preparation of *N*-Hydroxy-2,4,6-trinitroaniline (1a).** 2,4,6-Trinitroanisole (4.86 g, 0.02 mol) and hydroxylamine sulfate (1.97 g, 0.024 mol) were dissolved in dry, freshly distilled methanol (20 mL). Sodium methoxide solution (0.50 g of sodium (0.0217 mol) in 15 mL of dry methanol) was added with stirring at ambient temperature (dry nitrogen atmosphere maintained throughout). The very dark red solution was stirred for 18 h at ambient temperature. Concentrated sulfuric acid (6 drops) was added to dispel the red color, and the resultant orange solution was evaporated to dryness at room temperature. The residue was triturated with water acidified to pH 2 with sulfuric acid (100 mL), and the product was filtered off and washed with acidified water to leave an orange solid (4.83 g, 99%, mp 104–107 °C dec). Recrystallization by dissolving the product in 40 mL of methanol, followed by dilution with 40 mL of water acidified to pH 2 with sulfuric acid, and cooling to 0 °C gave large orange prisms of *N*-hydroxy-2,4,6-trinitroaniline (1): mp 100–103 °C dec (90% recovery) (lit.[16] mp 113 °C); IR 3350, 3250 (m, OH, NH), 1600, 1520, 1420 (s, $NO_2$), 1190, 925, 735, 725 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 8.89 (s, aromatic protons).

Anal. Calcd for $C_6H_4N_4O_7$: C, 29.52; H, 1.65; N, 22.95. Found: C, 29.57; H, 1.70; N, 22.83.

**Ozone Oxidation of *N*-Hydroxy-2,4,6-trinitroaniline (1a) to 1,2,3,5-Tetranitrobenzene (2).** *N*-Hydroxy-2,4,6-trinitroaniline (0.50 g, 2.05 mmol) was dissolved in boiling methylene chloride (250 mL). The clear yellow solution was then cooled to 0–5 °C in an ice bath, and ozone gas was bubbled through the stirred solution. The progress of the reaction was monitored by TLC (silica/methylene chloride). After 15 min, the reaction was complete and TLC showed only a single product. Nitrogen gas was bubbled through the solution, which was then evaporated to dryness to give a yellow solid (0.53 g, 100%). Recrystallization from chloroform gave 1,2,3,5-tetranitrobenzene (0.155 g) as yellow plates, mp 125–129 °C (lit.[9b] mp 127–129 °C). A parallel experiment in which the methylene chloride was predried over Drierite and molecular sieves (4A activated at 320 °C) were added to the reaction mixture prior to oxidation with ozone gave an identical result.

Similar procedures (omitting molecular sieves) were employed for the ozone oxidations of *N*-methoxy-2,4,6-trinitroaniline (**1b**) to **2**, *N*-methoxy-3-bromo-2,4,6-trinitroaniline (**5**) to 2,3,4,6-tetranitro-1-bromobenzene (**6**), *N*-methoxy-2,4-dinitro-3-methoxyaniline (**19**) to 1,2,6-trinitroanisole (**20**), and *N*-hydroxy-3,5-dinitroaniline (**21**) to 1,3,5-trinitrobenzene (**22**) (see Table I).

**Preparation of *N*-Methoxy-2,4,6-trinitroaniline (1b).** 2,4,6-Trinitrochlorobenzene (2.46 g, 20 mmol) and methoxyamine hydrochloride (1.67 g, 20 mmol) were dissolved in absolute ethanol (100 mL) at room temperature, and sodium bicarbonate (2.52 g, 30 mmol) was added in one portion with stirring. A deep red color developed immediately. After 10 min TLC (silica/methylene chloride) indicated that reaction was complete, and the red color was discharged by acidifying with 70% sulfuric acid. Evaporation of the solvent under reduced pressure gave a solid yellow mass, which was extracted with boiling benzene (2 × 75 mL) to give 1 g of a yellow solid. Recrystallization from benzene gave *N*-methoxy-2,4,6-trinitroaniline (**1b**) as yellow crystals (0.85 g, 33%), mp 140–141 °C dec. Recrystallization from chloroform increased the melting point to 150–152 °C dec: IR 3250 (m, NH), 1590, 1540, 1520, 1340, 1325 (s, $NO_2$), 1285 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.50 (s, 1 H, NH), 3.85 (s, 3 H, OMe), 9.10 (s, 2 H, aromatic).

**Preparation of *N*-Methoxy-3-bromo-2,4,6-trinitroaniline (5).** 2,4-Dibromo-1,3,5-trinitrobenzene[14] (7.44 g, 20 mmol) was dissolved in hot absolute ethanol (100 mL), and the solution was cooled to 40 °C. Methoxyamine hydrochloride (3.36 g, 40 mmol) was added and then sodium bicarbonate (6.72 g, 80 mmol) was added with stirring over 3 min. The reaction mixture was stirred for 1 h at ambient temperature, poured over crushed ice (75 g) to give a deep red solution, and then acidified with 1 N $H_2SO_4$ to give a voluminous yellow precipitate. The precipitate was filtered off and dissolved in chloroform (300 mL), and the chloroform solution was filtered through a phase-separating paper to remove residual water. Evaporation to dryness followed by recrystallization from chloroform gave *N*-methoxy-3-bromo-2,4,6-trinitroaniline (**5**) (orange needles, 2.08 g, 31%): mp 107 °C dec; IR 3150 (m, NH), 1580, 1540, 1520 (s, $NO_2$), 1305, 1250, 1220, 950, 905 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 3.77 (s, 3 H, OMe), 8.97 (s, 1 H, aromtic proton), 10.51 (br s, 1 H, NH).

Anal. Calcd for $C_7H_5BrN_4O_7$: C, 24.94; H, 1.50; Br, 23.71; N, 16.62. Found: C, 25.29; H, 1.44; Br, 23.63; N, 16.48.

**Preparation of *N*,*N*′-Dimethoxy-2,4-diamino-1,3,5-trinitrobenzene (7).** 2,4-Dibromo-1,3,5-trinitrobenzene[14] (1.0 g, 2.7 mmol) was dissolved in acetonitrile (50 mL). Methoxyamine hydrochloride (1.13 g, 13.5 mmol) was added followed by the addition of water (10 mL) to give a two-phase system. Sodium bicarbonate (1.14 g, 13.5 mmol) was added, with stirring, in one portion at room temperature. The initially deep red solution was stirred at ambient temperature for 7 h, leaving a clear orange solution. The organic layer was separated and evaporated to a red solid. The red solid was extracted with boiling chloroform (75 mL), leaving some residual sodium bromide. The clear orange filtrate was concentrated to 15 mL and cooled to ambient temperature, giving *N*,*N*′-dimethoxy-2,4-diamino-1,3,5-trinitrobenzene (golden plates, 0.50 g, 61%): mp 122–126 °C dec; IR 3250 (m, NH), 1600, 1550 (s, $NO_2$), 1400 (m), 1250, 1200 $cm^{-1}$ (s); NMR ($CD_3COCD_3$) 3.90 (s, 6 H, $OCH_3$), 9.03 (s, 1 H, aromatic).

Anal. Calcd for $C_8H_9N_5O_8$: C, 31.69; H, 2.99; N, 23.10. Found: C, 31.67; H, 2.97; N, 22.89.

**Preparation of 2,3,4,6-Tetranitro-1-bromobenzene (6).** *N*-Methoxy-3-bromo-2,4,6-trinitroaniline (2.55 g, 8 mmol) was dissolved in methylene chloride (200 mL) and cooled to 5 °C with stirring to give a clear orange solution. Ozone gas was bubbled through the solution for 2 h, during which time the solution lightened in color. At this time thin-layer chromatography (silica/methylene chloride) indicated the absence of starting material. The solution was purged of ozone by using oxygen and then evaporated to dryness to give a yellow oil (2.7 g). Crystallization twice at −20 °C from chloroform (5 mL) gave 2,3,4,6-tetranitro-1-bromobenzene (yellow prisms, 1.34 g, 53%): mp 113–114 °C; IR 1550 (s, $NO_2$), 1360 (m), 1320 (s, $NO_2$), 900 (m), 855 (m), 710 $cm^{-1}$ (m); NMR ($CDCl_3$) 8.71 (s, aromatic).

Anal. Calcd for $C_6HBrN_4O_8$: C, 21.38; H, 0.30; Br, 23.71; N, 16.63. Found: C, 21.56; H, 0.36; Br, 23.49; N, 16.44.

**Improved Synthesis of Pentanitroaniline (10).** Pentanitroaniline was prepared by nitration of 3,5-dinitroaniline by using a modification of the method of Flürscheim.[16] 3,5-Dinitroaniline (2.0 g, 11 mmol) was dissolved in 100% sulfuric acid (80 mL) and coolled to 5 °C. One hundred percent nitric acid (5 mL, 7.6 g, 120 mmol) was added dropwise over 10 min, during which time the temperature was held below 8 °C. The reaction mixture was then heated for 1 h at 70–75 °C and finally cooled in an ice bath. The yellow solid was filtered, air-dried at the pump for 10 min, and then dissolved in dichloroethane (70 mL). The organic layer was carefully decanted from the residual sulfuric

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[16] Flürscheim, B.; Holmes, E. L. *J. Chem. Soc.* **1928**, 3041.

acid, concentrated to 25 mL, and allowed to crystallize at −20 °C overnight to give pentanitroaniline (clear yellow plates, 1.46 g, 52%), mp 192–200 °C dec (lit.[9b] mp 193–202 °C).

**Ozone Oxidation of Pentanitroaniline in Oleum.** Pentanitroaniline (1.00 g, 3.1 mmol) was dissolved in 30% oleum (65 mL). Ozone gas was bubbled into the stirred solution for 48 h at ambient temperature. The reaction mixture was purged with oxygen and extracted with methylene chloride (5 × 100 mL). The combined extracts were dried over anhydrous magnesium sulfate and evaporated to give hexanitrobenzene (0.85 g, 78%) as a yellow solid. Recrystallization from pure dry chloroform gave chunky yellow prisms (mp 245–260 °C) identical with authentic hexanitrobenzene.[9b] In a similar manner, 2,4,6-trinitroaniline (**14**) was oxidized to **2**. The crude product, which was contaminated with ca. 5% **14** and 2,4,6-trinitrophenol (**15**), was recrystallized from chloroform (Table II).

**Ozone Oxidation of 4-Amino-2,3,5,6-tetranitrotoluene (12) to Pentanitrotoluene (13).** 4-Amino-2,3,5,6-tetranitrotoluene[17] (0.60 g, 2 mmol) was dissolved in 15% oleum (65 mL), and ozone gas was bubbled into the stirred solution for 48 h at ambient temperature. The reaction mixture was purged with oxygen and extracted with methylene chloride (5 × 100 mL). The acid solution was quenched on ice (200 g) and extracted with methylene chloride (5 × 100 mL). The combined extract was dried over anhydrous magnesium sulfate and evaporated to give pentanitrotoluene (0.38 g, 57%) as a yellow/orange solid. Recrystallization from pure, dry chloroform gave yellow needles, mp 225–240 °C dec, identical with authentic pentanitrotoluene.[9b]

**Preparation of *N*-Acetyl-2,4,6-trinitroaniline (16).** 2,4,6-Trinitroaniline (3.0 g, 13.2 mmol) was added to acetic anhydride (20.4 g, 200 mmol) with stirring, and several drops of 96% sulfuric acid were added. The reaction mixture was heated under reflux with stirring for 15 min and allowed to cool to ambient temperature. The off-white precipitate was filtered off and washed with ether. The filtrate was poured over crushed ice (100 g) and the resultant precipitate was filtered off and dried at the pump overnight. The combined solid materials were recrystallized from ethanol to give *N*-acetyl-2,4,6-trinitroaniline (white solid, 2.55 g, 69%): mp 233–235 °C (lit.[17] mp 235 °C); IR 3200 (m, NH), 1675 (s, CO), 1600 (s), 1540, 1500 (s, $NO_2$), 1330 (s, $NO_2$), 715 $cm^{-1}$ (s); NMR ($Me_2SO$-$d_6$) 2.12 (s, 3 H, $CH_3$), 9.05 (s, 2 H, aromatic), 11.05 (br s, 1 H, NH).

**Ozone Oxidation of *N*-Acetyl-2,4,6-trinitroaniline (16) to 1,2,3,5-Tetranitrobenzene (2).** 2,4,6-Trinitroacetaniline (1.1 g, 4.1 mmol) was dissolved in 10% oleum (65 mL), and ozone gas was bubbled into the stirred solution for 72 h at ambient temperature. The reaction mixture was purged with oxygen and extracted with methylene chloride (5 × 100 mL), and the extracts were dried over anhydrous magnesium sulfate and evaporated to give a yellow solid (0.30 g, 29%) identified by NMR as 1,2,3,5-tetranitrobenzene contaminated with about 5% 2,4,6-trinitroaniline and 2,4,6-trinitrophenol. Recrystallization from pure, dry chloroform gave yellow needles, mp 125–129 °C dec, identical with authentic 1,2,3,5-tetranitrobenzene.[9b]

**Preparation of *N*,*N*′-Diacetyl-2,4-diamino-1,3,5-trinitrobenzene (18).** 2,4-Diamino-1,3,5-trinitrobenzene (3.0 g, 12.3 mmol) was added to acetic anhydride (20.4 g, 200 mmol), with stirring, and several drops of 96% sulfuric acid were added. The reaction mixture was stirred at ambient temperature for 2 h, during which time the bright yellow color paled to give a white paste. The solid product was filtered off, washed with ether, and then dried at the pump to give *N*,*N*′-diacetyl-2,4-diamino-1,3,5-trinitrobenzene as a white solid (3.70 g, 92%): mp >330 °C dec; IR 3150 (m, NH), 1650 (s, CO), 1510, 1475 (s, $NO_2$), 1325 (s, $NO_2$), 1230 (m), 710 $cm^{-1}$ (m); NMR ($Me_2SO$-$d_6$) 2.05 (s, 6 H, $CH_3$), 8.84 (s, 1 H, aromatic), 10.92 (br s, 2 H, NH).

***N*-Methoxy-2,4-dinitro-3-methoxyaniline (19).** 2,3,6-Trinitroanisole (0.243 g, 1 mmol) in 10 mL of dry methanol was treated with excess methoxyamine (prepared by mixing 0.53 g (6.3 mmol) of methoxyamine hydrochloride with 0.32 g (6.0 mmol) of sodium methoxide in 10 mL of methanol). The reaction mixture was stirred under nitrogen at 25 °C for 16 h and then concentrated to dryness at reduced pressure. The residue was extracted with methylene chloride, and the extracts were concentrated to yield 0.23 g of an orange solid. Recrystallization from carbon tetrachloride gave 0.10 g (41%) of **19**, as orange red prisms: mp 105–107 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 8.12, 7.10 (AB q, $J$ = 10 Hz, 2 H), 4.05 (s, $CH_3$), 3.80 (s, $CH_3$).

Anal. Calcd for $C_8H_9N_3O_6$: C, 39.51; H, 3.73; N, 17.28 ($M_r$ 243.18). Found: C, 39.62; H, 3.78; N, 17.19 ($M_r$ 243 (MS)).

**2,3,6-Trinitroanisole (20).** To 2,3,6-trinitrophenol (2.29 g, 0.01 mol)[18] in 30 mL of diethyl ether was added an ether solution of diazomethane (prepared from 0.02 mol of (*p*-tolylsulfonyl)methylnitrosamide). The reaction temperature was maintained below 5 °C by cooling with an ice bath. After standing at 25 °C for 2 h, the ether and excess diazomethane were distilled off under reduced pressure to yield 2.31 g (95%) of **20**. Recrystallization from carbon tetrachloride gave chunky prisms: mp 28–29 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 8.13, 8.10 (AB q, $J$ = 8 Hz, 2 H), 4.10 (s, $CH_3O$).

Anal. Calcd for $C_7H_5N_3O_7$: C, 34.58; H, 2.07; N, 17.28 ($M_r$ 243.13). Found: C, 34.62; H, 2.10; N, 17.18 ($M_r$ 243 $M^+$ (MS)).

**Registry No.** **1a**, 18631-76-0; **1b**, 24914-56-5; **2**, 3698-53-1; **5**, 88106-03-0; **6**, 88106-04-1; **7**, 88106-05-2; **10**, 21985-87-5; **11**, 13232-74-1; **12**, 84432-53-1; **13**, 73334-00-6; **14**, 489-98-5; **16**, 16400-86-5; **17**, 88106-06-3; **19**, 88106-07-4; **20**, 88106-08-5; **21**, 88106-09-6; **22**, 99-35-4; ozone, 10028-15-6; peroxydisulfuric acid, 13445-49-3; 2,4,6-trinitroanisole, 606-35-9; 2,4,6-trinitrochlorobenzene, 88-88-0; 2,4-dibromo-1,3,5-trinitrobenzene, 13506-78-0; 3,5-dinitroaniline, 618-87-1; 2,4-diamino-1,3,5-trinitrobenzene, 1630-08-6; 2,3,6-trinitrophenol, 603-10-1.

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(18) Reverdin, F.; Meldola, R. *J. Prakt. Chem.* **1913**, *88*, 785.