

Synthesis of Polynitro Compounds. Peroxydisulfuric Acid Oxidation of Polynitroarylamines to Polynitro Aromatics¹

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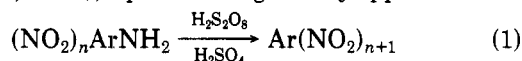
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Peroxydisulfuric acid in sulfuric acid solution, prepared by reaction of hydrogen peroxide with excess oleum or 100% H₂SO₄, oxidizes primary polynitroarylamines and their *N*-acetamido derivatives to polynitro aromatics in good to excellent yields. The new procedure is illustrated by the synthesis of several new polynitro compounds, not preparable by known synthetic methods. Peroxytrifluoromethanesulfonic acid is comparably efficient for such oxidations. The scope and limitations of the new reaction have been examined and compared to other methods of synthesis of polynitro compounds.

Direct oxidation of amines is very useful for the preparation of nitro compounds.³ It is convenient, owing to the availability and stability of the required amines, the simplicity of the procedures, and the high yields and purity of isolated products. However, most of the known oxidation methods of this type suffer from rather limited scope. The present work reports a new method which converts primary polynitroarylamines to polynitro aromatics (eq 1, $n > 1$), a process not generally applicable with



previously described procedures. New polynitro aromatics, not preparable by any other known method, may be synthesized. Peroxydisulfuric acid, conveniently prepared by the addition of 90–98% hydrogen peroxide to oleum or 100% H₂SO₄, has been found to readily oxidize an amine such as pentanitroaniline to hexanitrobenzene.⁴ The scope and limitations of this new reaction have been examined, and our results are now described in this report. Comparisons are briefly made with some related methods of synthesis of polynitro compounds.

Several oxidants, principally peracids, have previously been employed in the direct NH₂ → NO₂ conversion. Peracids include Caro's acid (peroxysulfuric acid, H₂SO₅)⁵ and peracetic,⁶ peroxytrifluoroacetic,⁷ peroxymaleic,⁸ *m*-

chloroperbenzoic,⁹ and perbenzoic¹⁰ acids. Although the scope and limitations of these oxidations have not been completely established, some general observations may be noted. The power of the oxidant is proportional to the acid strength of the deoxy peracid. Peracetic and *m*-chloroperbenzoic acids are suitable for oxidation of aliphatic primary amines. Peracetic, peroxytrifluoroacetic, and peroxymaleic acids are best for oxidation of various ring-substituted anilines, although certain anilines with electron-releasing groups such as alkoxy are destroyed by peroxytrifluoroacetic acid. Caro's acid has been employed for oxidation of aminopyridines (*N*-oxides sometimes result);^{5d–g} with anilines one often obtains nitroso compounds, although more vigorous conditions can yield the nitro product.^{5a–c} Other oxidants of preparative value include potassium permanganate (for aliphatic tertiary carbinamines only)¹¹ and ozone.¹²

One notable limitation of the known amine oxidants is their failure to oxidize amino to nitro in polynitroarylamines having more than two nitro groups attached to one benzene ring. There is only one recorded example of this type—the conversion of 3-amino-2,4,6-trinitrotoluene to 2,3,4,6-tetranitrotoluene (85% yield) by potassium persulfate in concentrated sulfuric acid at 100 °C;^{5a} this oxidant will not oxidize picramide to 1,2,3,5-tetranitrobenzene under the same conditions. One of the most powerful peracid oxidants, peroxytrifluoroacetic acid, will efficiently oxidize dinitroanilines to the corresponding trinitrobenzenes but not trinitroanilines to tetranitrobenzenes;⁷ it will oxidize pentafluoroaniline to pentafluoronitrobenzene (85% yield).^{7d}

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(3) Brief reviews of the oxidation of amines to nitro compounds have been published: (a) "Methoden der Organischen Chemie (Houben-Weyl)", 4th ed; Georg Thieme Verlag: Stuttgart, 1971; Vol. X, Part 1, pp 104–106, 843–848. (b) Larson, H. O. In "The Chemistry of the Nitro and Nitroso Groups"; Feuer, H., Ed.; Interscience: New York, 1969; Part 1, pp 308–10. (c) Weaver, W. M. *Ibid.* 1970; Part 2, pp 29–31.

(4) Nielsen, A. T.; Atkins, R. L.; Norris, W. P. *J. Org. Chem.* 1979, 44, 1181.

(5) (a) Holleman, A. F. *Recl. Trav. Chim. Pays-Bas* 1930, 49, 501. (b) Witt, O. N.; Kopetschni, E. *Ber. Dtsch. Chem. Ges.* 1912, 45, 1134. (c) Bradley, W.; Leete, E. *J. Chem. Soc.* 1951, 2129. (d) Wiley, R. H.; Hartman, J. L. *J. Am. Chem. Soc.* 1951, 73, 494. (e) Brown, E. V. *Ibid.* 1957, 79, 3565. (f) Herz, W.; Murty, D. R. K. *J. Org. Chem.* 1961, 26, 122, 418. (g) Kirpal, A.; Böhm, W. *Ber. Dtsch. Chem. Ges.* 1932, 65, 680.

(6) (a) Emmons, W. D. *J. Am. Chem. Soc.* 1957, 79, 5528. (b) Holmes, R. R.; Bayer, R. P. *Ibid.* 1960, 82, 3454. (c) Mosby, W. L.; Berry, W. L. *Tetrahedron* 1959, 5, 93. (d) Gilbert, E. E.; Leccacorvi, J. R. *Propellants Explos.* 1976, 1, 89. (e) Gilbert, E. E. *Synthesis* 1977, 315.

(7) (a) Emmons, W. D. *J. Am. Chem. Soc.* 1954, 76, 3470. (b) Dennis, W. H., Jr.; Rosenblatt, D. H.; Blucher, W. G.; Coon, C. L. *J. Chem. Eng. Data* 1975, 20, 202. (c) Khmel'nitskii, L. I.; Novikova, T. S.; Novikov, S. S. *Izv. Akad. Nauk SSSR* 1962, 516. (d) Brooke, G. M.; Burdon, J.; Tatlow, J. C. *J. Chem. Soc.* 1961, 802. (e) Pagano, A. S.; Emmons, W. D. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 367.

(8) White, R. W.; Emmons, W. D. *Tetrahedron* 1962, 17, 31.

(9) (a) Gilbert, K. E.; Borden, W. T. *J. Org. Chem.* 1979, 44, 659. (b) Robinson, C. H.; Milewich, L.; Hofer, P. *Ibid.* 1966, 31, 524.

(10) Nysted, L. N.; Burtner, R. R. *J. Org. Chem.* 1962, 27, 3175.

(11) (a) Kornblum, N.; Clutter, R. J.; Jones, W. J. *J. Am. Chem. Soc.* 1956, 78, 4003. (b) Kornblum, N.; Jones, W. J. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, 845.

(12) (a) Bachman, G. B.; Strawn, K. G. *J. Org. Chem.* 1968, 33, 313. (b) Keinan, E.; Mazur, Y. *Ibid.* 1977, 42, 844.

It is evident that the weaker the basicity (and nucleophilicity) of the amino group, the more powerful must be the oxidant required to convert it into a nitro group. Furthermore, these two parameters (amine nucleophilicity and oxidant power) must be carefully matched in a particular system so as to avoid excessive oxidation and destruction of the substrate on the one hand and complete absence of oxidation on the other. Unfortunately, amine basicity alone cannot direct selection of the optimum oxidant. For example, 2-aminonaphthalene ($pK = 4.15$ at 25°C) is a weaker base than *p*-toluidine ($pK = 4.72$), yet the naphthalene derivative is oxidatively destroyed by peroxytrifluoroacetic acid whereas the toluidine provides a 78% yield of 4-nitrotoluene under the same conditions.^{7a}

Peroxydisulfuric acid itself is believed not to have been the oxidant employed in previously reported oxidations of an amino to a nitro group. Its salts, potassium or ammonium persulfate, have been employed in sulfuric acid solutions of various concentrations, including 96% H_2SO_4 .^{5a-c} These solutions, as employed, contain Caro's acid (peroxymonosulfuric acid, H_2SO_5) but not peroxydisulfuric acid. Oxidations with 30% hydrogen peroxide in sulfuric acid, as reported, also involve Caro's acid.^{5d-g} Peroxydisulfuric acid when produced in these solutions containing water forms peroxymonosulfuric acid very rapidly, especially when heated¹³ (eq 2).



Peroxydisulfuric acid is one of the most powerful known oxidants ($\text{S}_2\text{O}_8^{2-} + 2e^- \rightarrow 2\text{SO}_4^{2-}$; $E^0 = 2.01\text{ V}$).^{13b} It is conveniently prepared by reaction of 90–98% hydrogen peroxide with a large excess of oleum or 100% H_2SO_4 at 25°C (see eq 3 and 4). The formation of H_2SO_5 is slow

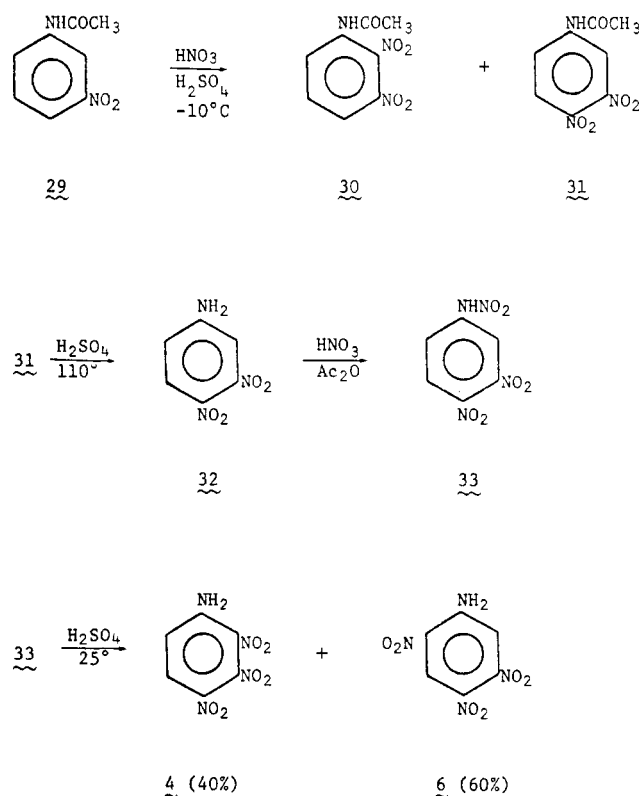


under these conditions since the water concentration is very low or zero and the temperature is low. The amine to be oxidized is dissolved in excess oleum or 100% H_2SO_4 (1–2% solutions are commonly employed in the present study, owing to the limited solubility of the reactants). The solution is treated with a very large excess of 98% H_2O_2 (molar ratio ca. 50:1), keeping the temperature below $25\text{--}30^\circ\text{C}$. Under these conditions the reaction rate is often slow with the reactants listed in Table I, and a reaction time of 18–24 h (at $25\text{--}30^\circ\text{C}$) is employed to ensure completion of the oxidation; the product is stable under these conditions. The large excess of H_2O_2 increases the reaction rate in the dilute solutions and assures a high concentration of $\text{H}_2\text{S}_2\text{O}_8$ throughout the reaction, as it slowly undergoes some decomposition; with smaller amounts of H_2O_2 the reaction rate is slower, the yield lower, and the nitro product sometimes less pure. Prolonged heating of the reaction mixture above $35\text{--}40^\circ\text{C}$ to increase the rate is avoided since it may lead to sudden vigorous decomposition with violent gassing. The nitro product is conveniently isolated by filtration if it precipitates out or by extraction with methylene chloride if it remains in solution; unreacted amine may sometimes be recovered by quenching the product-free sulfuric acid solution in ice.

At the outset of this investigation two polynitrobenzenes were unknown (pentanitrobenzene and 1,2,3,4-tetranitrobenzene) and one, hexanitrobenzene, had been reported without a description of its method of synthesis.¹⁴ The

(13) (a) Ullrich, F. *J. Prakt. Chem.* **1939**, [2] 153, 91. (b) "Gmelin Handbuch der Anorganischen Chemie, Sulfur B2", 8th ed.; 1960; pp 803, 825.

Scheme I



preparations of pentanitrobenzene and hexanitrobenzene by peroxydisulfuric acid oxidation of 2,3,4,6-tetranitroaniline and pentanitroaniline, respectively, are described in a previous paper.⁴ [An improved procedure for nitration of 3,5-dinitroaniline to pentanitroaniline is described in the Experimental Section of this report. Addition of a lead salt to the nitration mixture facilitates rearrangement of nitramine intermediates to *C*-nitro products.¹⁵]

The known tetranitrobenzenes (1,2,3,5 and 1,2,4,5 isomers) have been prepared by Borsche and co-workers by nitric acid oxidation of hydroxylamine precursors.¹⁶ Picrylhydroxylamine was oxidized to 1,2,3,5-tetranitrobenzene (56% yield of crude)^{16a} and 2,4-bis(hydroxyamino)-1,5-dinitrobenzene to 1,2,4,5-tetranitrobenzene (yield not stated).^{16b,c} Holleman prepared 1,2,3,5-tetranitrobenzene by reaction of 2,4,6-trinitrobenzenediazonium nitrate with sodium nitrite (64–69% yield).¹⁷ These methods are not readily applicable to the synthesis of polynitro aromatics such as the previously unreported 1,2,3,4-tetranitrobenzene. Synthesis of the required relatively unstable hydroxylamine intermediates is sometimes difficult. The diazotization reaction cannot be applied to synthesis of those polynitro aromatics (such as hexanitrobenzene) which are sensitive to water and other nucleophiles.

The peroxydisulfuric acid oxidation of trinitroanilines in 100% sulfuric acid represents a convenient direct synthetic route leading to the corresponding tetranitrobenzenes in excellent yield (Table I). Yields are higher

(14) (a) Akopyan, Z. A.; Struchkov, Y. T.; Dashevskii, V. G. *Zh. Strukt. Khim.* **1966**, 7, 408. (b) Orlova, E. Y. "Chemistry and Technology of High Energy Explosive Substances"; Khimia: Leningrad, 1973; p 140.

(15) Lothrop, W. C.; Handrick, G. R.; Hainer, R. M. *J. Am. Chem. Soc.* **1951**, 73, 3581.

(16) (a) Borsche, W. *Ber. Dtsch. Chem. Ges.* **1923**, 56, 1494, 1939. (b) Borsche, W.; Feske, E. *Ibid.* **1926**, 59, 815. (c) Crampton, M. R.; El Ghariani, M. *J. Chem. Soc. B* **1970**, 391.

(17) Holleman, A. F. *Recl. Trav. Chim. Pays-Bas* **1930**, 49, 112.

in 100% H₂SO₄ than in oleum. The 1,2,3,5 isomer **19** was obtained in 93% yield by oxidation of picramide (**5**); in 20% oleum the yield was 62%. 2,4,5-Trinitroaniline (**6**) gave 1,2,4,5-tetranitrobenzene (**20**) in 83% yield. 1,2,3,4-Tetranitrobenzene (**18**), the new isomer, was obtained by oxidation of 2,3,4-trinitroaniline (**4**) (78% yield).

2,3,4- and 2,4,5-trinitroanilines, the tetranitrobenzene precursors, were prepared as outlined in Scheme I.^{18,19} Improved and/or new methods and procedures were developed for each step (**29** → **30** + **31**; **31** → **32** + **33**; **33** → **4** + **6**). Reaction of 3,4-dinitroaniline (**32**) with acetyl nitrate at 25 °C gave nitramine **33** (76% yield), previously reported to form from **31** in very low yield.¹⁹ The acid-catalyzed rearrangement of nitramine **33** in concentrated H₂SO₄ gave a mixture containing only 2,3,4-trinitroaniline (**4**, 40%) and 2,4,5-trinitroaniline (**6**, 60%). Macciotta^{19b} employed nitramine **33** as its mercury salt in the acid-catalyzed rearrangement in sulfuric acid to obtain a mixture of **4** (30%) and **6** (70%).

1,2,3-Trinitrobenzene (**16**) was prepared by oxidation of 2,6-dinitroaniline (**2**) in concentrated sulfuric acid (96% H₂SO₄) by the usual procedure of addition of 98% H₂O₂ to the acid solution of the amine (56% yield). The same reaction conducted in 20% oleum gave recovered amine but no trinitrobenzene. Dinitroanilines are more efficiently oxidized to trinitrobenzenes by peroxytrifluoroacetic acid⁷ (92% yield of **16** from **2**^{7c}). Mononitroanilines are readily oxidized to the dinitro products with peracetic^{6d} or peroxytrifluoroacetic acid.^{7a}

Dinitro- and trinitrotoluenes have been obtained in yields of 70–100% by peroxytrifluoroacetic acid oxidation of the corresponding nitro- and dinitrotoluidines, respectively.^{7a,b} However, the oxidation of trinitrotoluidines to tetranitrotoluenes requires a more powerful oxidant. 3-Amino-2,4,6-trinitrotoluene (**7**) has been oxidized to 2,3,4,6-tetranitrotoluene (**21**) in 74% yield with Caro's acid^{5a} and by peroxydisulfuric acid (82% yield) in the present work (Table I). The two isomers 2,3,4,5- and 2,3,5,6-tetranitrotoluene, remain unknown, as do their trinitrotoluidine precursors.

Pentanitrotoluene (**28**) has not been described previously; the potential tetranitrotoluidine precursors are also unknown. In the present work **28** was prepared in 54% yield by peroxydisulfuric acid oxidation of 3,5-bis(di-acetylamino)-2,4,6-trinitrotoluene (**14**). The reaction of 3,5-diacetamido-2,4,6-trinitrotoluene with peroxydisulfuric acid under the same conditions gave only a trace of **28**.

The diamine 3,5-diamino-2,4,6-trinitrotoluene was destroyed exothermically (fume off) by peroxydisulfuric acid in sulfuric acid. Other diaminopolynitroanilines, including 1,3-diamino-2,4,6-trinitrobenzene and 3,5-diamino-2,4,6-trinitrofluorobenzene, as well as the triamines 1,3,5-triamino-2,4,6-trinitrobenzene and melamine, are also destroyed exothermically by this oxidant.

The acetamido derivative, 3,5-diacetamido-2,4,6-trinitrofluorobenzene (**13**) was oxidized by peroxydisulfuric acid to pentanitrofluorobenzene (**27**, 20% yield). The use of acetamido derivatives of amines is not uniformly successful, however. 2,4,6-Triacetamido-1,3,5-triazine, acetanilide, and 3,6-diacetamido-1,2,4,5-tetrazine were decomposed by peroxydisulfuric acid in sulfuric acid. The milder oxidant, peracetic acid, has been employed in the oxidation

of acetanilide and some of its ring-substituted derivatives to the corresponding nitrobenzenes;²⁰ chromium trioxide in acetic acid has also been reported to effect this conversion.²¹

The new fluorinated polynitrobenzenes 1,3-difluoro-2,4,5,6-tetranitrobenzene (**17**) and 1,5-difluoro-2,3,4-trinitrobenzene (**15**) were readily prepared by peroxydisulfuric acid oxidation of the amines 3,5-difluoro-2,4,6-trinitroaniline (**3**) and 3,5-difluoro-2,6-dinitroaniline (**1**), respectively. On the other hand, 2,4,6-tribromoaniline was destroyed exothermically by the reagent.

The polycyclic compounds 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl (**11**) and 4,6-bis(3-amino-2,4,6-trinitrophenyl)-1,3-dinitrobenzene (**12**), each containing amino groups in separate rings, were oxidized in good yields by peroxydisulfuric acid to the corresponding polynitro aromatics 2,2',3,3',4,4',6,6'-octanitrobiphenyl (**25**) and the decanitro-*m*-terphenyl **26**, respectively. The oxidation of 3-amino-2,2',4,4',6,6'-hexanitrostilbene (**10**) occurred without epoxide formation, leading to the heptanitrostilbene **24**. However, the azo compound 3,3'-diamino-2,2',4,4',6,6'-hexanitroazobenzene was decomposed by peroxydisulfuric acid.

The scope and limitations of the peroxydisulfuric acid oxidation of amines to nitro compounds can be broadly outlined. Peroxydisulfuric acid in sulfuric acid is the most powerful of the known peracid oxidants, with the possible exception of peroxytrifluoromethanesulfonic acid (vide infra). It will oxidize the amino to a nitro group in trinitro-, tetranitro-, and pentanitroanilines, all of which are not acted upon by peroxytrifluoroacetic acid. Crude products, isolated in excellent yields, are usually very pure. Impurities such as azo, azoxy, or nitroso compounds, often contaminating the nitro products when weaker peracids are employed,^{5,6} are usually absent in the final products. Unreacted amine, if any, remains dissolved in the acid and is not present in the isolated product. Peroxydisulfuric acid is the reagent of choice for the oxidation of primary polynitro aromatic amines to polynitro aromatics. Its use is limited to very weakly basic amines, however. Dinitrotoluidines (4-amino-2,6-dinitrotoluene, 2-amino-3,5-dinitrotoluene, and 3-amino-2,6-dinitrotoluene) were not oxidized to trinitrotoluenes and were recovered (60–90%) in solvents of 96 and 100% sulfuric acid or 20% oleum. Similar results were obtained with 2,6-dinitroaniline in 20% oleum, although oxidation to the trinitrobenzene was achieved in 96% H₂SO₄. 2-Aminonaphthalene and melamine in 100% H₂SO₄ or 20% oleum also gave recovered reactant and no nitro product.

In some reactions peroxydisulfuric acid in oleum or 100% sulfuric acid attacked the reactant very vigorously, resulting in a very rapid temperature rise and fume off. Oxidation, involving conversion of a ring hydrogen to hydroxyl, followed by further rapid oxidation of the new substrate, is believed to occur. These events also result with polynitrophenylenediamines and with triamines. Testing of the oxidant in a new reaction should be attempted carefully with limited quantities of amine (100 mg or less) with adequate protection from fume off; no explosions have yet occurred under the reaction conditions herein described.

Use of *N*-acetyl or *N,N*-diacetyl derivatives of certain amines and diamines, rather than the free amine, is one method of decreasing reactant activity, thereby minimizing ring-oxidation reactions. The *N,N*-diacetyl derivatives appear to be superior for this purpose. A very slow ad-

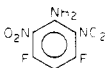
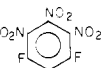
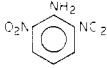
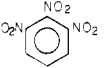
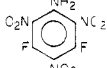
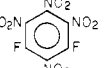
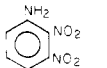
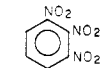
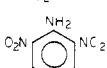
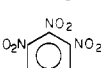
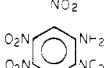
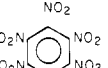
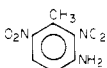
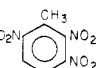
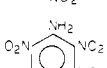
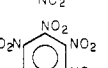
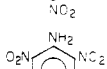
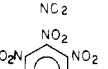
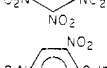
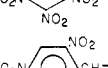
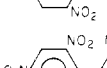
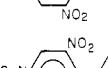
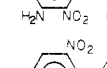
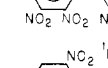
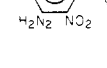
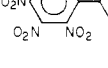
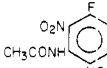
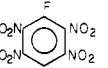
(18) (a) Wender, V. *Gazz. Chim. Ital.* 1889, 19, 225. (b) Kaufmann, A.; Hüsey, H. *Ber. Dtsch. Chem. Ges.* 1908, 41, 1735. (c) Van de Vliet, P. G. *Recl. Trav. Chim. Pays-Bas* 1924, 43, 606. (d) Welsh, L. H. *J. Am. Chem. Soc.* 1941, 63, 3276.

(19) (a) Macciotta, E. *Gazz. Chim. Ital.* 1931, 61, 773. (b) Macciotta, E. *Ibid.* 1941, 71, 81. (c) Oglobin, K. A.; Markina, G. V. *Zh. Obshch. Khim.* 1955, 25, 989.

(20) Bigiavi, D.; Albanese, C. *Gazz. Chim. Ital.* 1935, 65, 249.

(21) Hock, H.; Kropf, H. *Ber. Dtsch. Chem. Ges.* 1956, 89, 2436.

Table I. Peroxydisulfuric Acid Oxidation of Polynitroarylamines and Amides to Polynitro Aromatics

no.	reactant	H ₂ SO ₄ solvent concn, % ^a	no.	product ^b	yield, % ^c	mp, °C ^d (recryst solvent) ^e	¹ H NMR shifts, δ; solvent ^f
1		100	15		56	88-90 (CH ₂ Cl ₂ /hexane)	7.62 (t, <i>J</i> = 8.53 Hz); CD ₂ Cl ₂
2		96	16		56 (0) ^g	121-122 ^h (CH ₃ OH)	8.48 (d); 7.92 (t, <i>J</i> = 8.40 Hz); CDCl ₃
3		100	17		84	99-100 (CH ₂ Cl ₂ /hexane)	
4		100	18		78 (96) ⁱ	119-120 (CHCl ₃)	8.51 (s); CD ₂ Cl ₂
5		100	19		93 ^j (62) ^g	127-129 ^k (CHCl ₃)	9.35 (s); CD ₂ Cl ₂
6		100	20		83	190-191 ⁱ (CHCl ₃)	8.59 (s); CD ₂ Cl ₂
7		100	21		82	135-136.5 ^m (CHCl ₃)	9.00 (s, 1), 2.66 (s, 3); CDCl ₃ /acetone
8		104.5	22		85 ^j	142-143 (CHCl ₃)	9.15 (s); CDCl ₃
9		104.5	23		58 ^j (90) ⁿ	246-262 ^{j,o} (CHCl ₃)	
10		104.5	24		53	248 (CH ₂ Cl ₂ /acetone)	9.06 (s, 2), 8.71 (s, 1), 6.91 (s, 1), 6.89 (s, 1); (CD ₃) ₂ SO
11		104.5	25		96	245 (ClCH ₂ CH ₂ Cl)	8.76 (s); (CD ₃) ₂ SO
12		104.5	26		90	> 320 dec (CH ₃ CO ₂ C ₂ H ₅)	9.00 (s, 1), 8.82 (s, 2), 7.82 (s, 1); (CD ₃) ₂ SO
13		100	27		23	152-154 (CCl ₄)	
14		106.8	28		54	225-240 (CHCl ₃)	2.57 (s); CDCl ₃

^a Reactant dissolved in sulfuric acid (0.5-2% solution often limited by solubility) and treated with 90-98% H₂O₂ (25-30 °C, 18-24 h); solvents 96 and 100% H₂SO₄, 20% oleum (equivalent to 104.5% H₂SO₄) or 30% oleum (106.8% H₂SO₄).

^b Satisfactory elemental analyses (±0.4% for C, H, and N) were obtained for the new compounds listed. ^c Yields (not optimized) of high purity products. ^d Melting points of pure recrystallized samples with solvent listed. ^e Pure, anhydrous solvents. ^f Chemical shifts (δ) referenced to tetramethylsilane as internal standard (30 °C); ¹³C NMR data to be published separately. ^g Yield in 20% oleum. ^h Reported melting point of 121 °C.^{16a} ⁱ Yield based on unrecovered reactant.

^j Detailed results in ref 4. ^k Reported melting point: 125-126 °C;^{16a} 129-130 °C.¹⁷ ^l Reported melting point of 188 °C.^{16b} ^m Reported melting point of 136.5 °C.^{5a} ⁿ Yield with peroxytrifluoromethanesulfonic acid (this work).

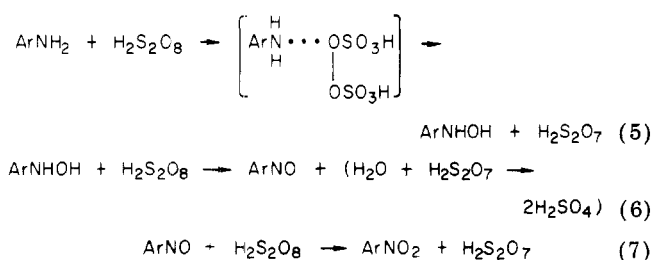
^o Reported melting point of 240-258 °C.^{14b} No procedure has yet appeared describing the preparation of hexanitrobenzene except in the present work and ref 4.

dition of hydrogen peroxide to the sulfuric acid solution of the reactant may be required to secure maximum yield. Although these modifications have not been examined extensively, the peroxydisulfuric acid oxidation of these amide derivatives represents an attractive alternative route to polynitro aromatics. Secondary amines, such as *N*-methylpolynitroarylamines, should be oxidizable to polynitro aromatics by peroxydisulfuric acid. This type of

reaction is effected by peroxytrifluoroacetic acid (*N*-methylaniline → nitrobenzene^{7a}).

A new oxidation reagent, peroxytrifluoromethanesulfonic acid, was prepared by reaction of 90-98% H₂O₂ with excess trifluoromethanesulfonic acid. It is possibly the most powerful of the peracid oxidants. It oxidized pentanitroaniline to hexanitrobenzene in 90% yield, compared to a 58% yield obtained with peroxydisulfuric acid. Although

Scheme II



we have not yet examined it extensively, it may prove valuable in some oxidation reactions where peroxydisulfuric acid is not sufficiently powerful. Potassium persulfate in anhydrous trifluoromethanesulfonic acid oxidized pentanitroaniline to hexanitrobenzene in 21% yield, whereas the same salt in 20% oleum gave no hexanitrobenzene.

The mechanism of oxidation of primary amines by peracids has been studied and reviewed.²²⁻²⁴ The reaction is considered to be a second-order nucleophilic attack by amine nitrogen on the electrophilic oxygen of the peracid. The reaction rate is accelerated by electron-releasing groups and retarded by electron-withdrawing groups (large negative ρ value). Stepwise oxidation of primary amino to nitro occurs via hydroxylamine and nitrosoamine intermediates (Scheme II). Peracid attack on the free amine rather than its salt is supported by our observation that oxidation of the more basic amines occurs in less concentrated acid (96%), but not in 100% H_2SO_4 or oleum, whereas only the most weakly basic amines are oxidized by $\text{H}_2\text{S}_2\text{O}_8$ in oleum. Greenish nitroso compounds are evident in early stages of the reaction, and these substances may color the product when a lower molar ratio of oxidant is employed. The oxidizing power of a peracid is related to the acid strength of the conjugate acid of the departing anion. Peracid reduction products are the corresponding deoxy acids, which from $\text{H}_2\text{S}_2\text{O}_8$ is probably pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$ (a stronger acid than H_2SO_4 ²⁵). Solvent (H_2SO_4)-mediated proton-transfer steps are assumed to be involved in each step of Scheme II, and these are facilitated by the very high acidity of the medium.²⁶

Experimental Section

Caution! The polynitro compounds described herein are powerful explosives and should be handled carefully. The reagent peroxydisulfuric acid in sulfuric acid solution is a very powerful oxidant which may react violently with many organic materials, especially when heated. New reactions in which it is employed should first be tested on small quantities (100 mg of substrate or less) with adequate safety precautions. Used peracid solutions should be disposed of immediately after workup by cautiously flushing with plenty of water. Concentrated H_2O_2 (90–98%), a powerful oxidant, must be handled with extreme care.^{7e}

3,5-Dinitroaniline was prepared from 3,5-dinitrobenzoic acid (Aldrich) by a modification of the procedure of Lothrop and co-workers.¹⁵ It was found that with the specified chloroform solvent it was necessary to extend the reported reflux time of 3 h to 12–14 h in order to completely decompose the acyl azide

intermediate. Alternatively, the reaction mixture could be heated to 80 °C without the chloroform, or it could be heated with 1,2-dichloroethane to raise the reaction temperature to ca. 83 °C, using a reflux period of 3 h; the crude product melted at 158–162 °C (70–90% yield); one recrystallization from ethanol gave prisms, mp 161–163 °C (60% recovery) (lit.¹⁵ mp 162–163 °C).

Pentanitroaniline (9). To a mixture of 250 mL of 30% oleum and 300 mL of concentrated H_2SO_4 was added 1.0 g of red lead oxide, Pb_3O_4 , and 18.3 g (0.1 mol) of 3,5-dinitroaniline with stirring, keeping the temperature below 25 °C by ice-bath cooling until a clear solution was obtained (10 min). A solution of 90% HNO_3 (50 mL, 1.07 mol) in 100 mL of concentrated H_2SO_4 was then added dropwise with stirring during 10 min, keeping the temperature below 30 °C. The mixture was then heated and stirred in a hot water bath and the temperature raised from 30 to 70 °C during 30 min, followed by heating and stirring for 1.25 h at 70–75 °C. Without removal of the flask from the water bath, heating was discontinued, and the mixture was allowed to cool to 25 °C without stirring (15 h). The precipitated product was filtered through a sintered-glass funnel and washed successively with concentrated sulfuric acid, 50% aqueous sulfuric acid, and ice-water to yield 14.1 g (44.4%) of high purity, crystalline pentanitroaniline [9, mp 193–202 °C dec (lit.²⁷ mp 192 °C)] which was recrystallized from boiling 1,2-dichloroethane (400 mL) to give small yellow prisms: 10.2 g; mp 188–192 °C dec (some decomposition occurs during recrystallization). One sample of the crude product, recrystallized from benzene, gave chunky, bright yellow prisms, mp 210–211 °C dec. Anal. Calcd for $\text{C}_6\text{H}_2\text{N}_5\text{O}_{10}$: C, 22.65; H, 0.63; N, 26.42. Found: C, 22.70; H, 0.89; N, 26.20. All samples show identical infrared spectra in KBr (sharp NH_2 doublet at 3480 and 3590 cm^{-1} and absence of CH absorption).

Parallel runs gave yields of 43–49%. In runs in which a lead salt was omitted the yields of 9 were lower (35–40%). The solubility of lead sulfate in 100% H_2SO_4 is 1.8 g of lead sulfate/100 g of 100% H_2SO_4 at 25 °C.²⁸ Lead salts are absent in the crude product obtained by the above procedure.

2,3-Dinitroacetanilide (30) and 3,4-Dinitroacetanilide (31). 3-Nitroacetanilide²⁹ (64.8 g, 0.36 mol) was added to a mixture of 390 mL each of concentrated (96%) H_2SO_4 and nitric acid (90%) with stirring at –3 to –4 °C during 30 min (ice-salt bath cooling). After the mixture was stirred at –10 to –12 °C for 30 min, a clear yellow solution was obtained which was allowed to warm to 2 °C during 1 h without stirring. The solution was then stirred into 2.5 kg of crushed ice; the resulting yellow precipitate was filtered off and washed thoroughly with water. After being dried by suction for 45 min, the still moist filter cake was immediately dissolved in 600 mL of boiling absolute ethanol. Cooling overnight deposited 26.6 g of crude 30 (mp 165–182 °C) which was recrystallized from acetic acid (60 mL) to yield 16.9 g (21%) of 2,3-dinitroacetanilide (30), mp 188–190 °C (lit. mp 186–187,^{18b} 189.5–190 °C^{18d}). The ethanol filtrate remaining after removal of the crude 30 was concentrated to dryness under reduced pressure at 25 °C and the residue boiled with 400 mL of benzene; some solid remained undissolved. Without filtration the solution was cooled to 25 °C to deposit 26.6 g of crude 31 (mp 140–144 °C) which was recrystallized from benzene to yield 22.5 g (28%) of 3,4-dinitroacetanilide (31) as yellow prisms, mp 144.5–145.5 °C (lit. mp 144–145,^{18b} 146.5–147 °C^{18d}).

3,4-Dinitroaniline (32). 3,4-Dinitroacetanilide (31; 12.0 g, 0.0533 mol) was added with stirring during 2 min to 50 mL of concentrated H_2SO_4 held at 110 °C. After being heated at 110 °C for 5 min, the solution was immediately chilled in an ice bath and poured on crushed ice to yield 9.26 g (95%) of bright yellow crystals of 3,4-dinitroaniline (mp 153–154 °C) which was used without further purification (lit. mp 154,^{18a} 155–156 °C^{18d}).

N-Nitro-3,4-dinitroaniline (33). To 3,4-dinitroaniline (32; 4.0 g, 0.0218 mol) dissolved in 90 mL of acetic acid was added successively, with stirring, 5 mL of 90% HNO_3 and 5 mL of acetic anhydride (temperature rise from 25 to 38 °C). The solution was cooled, and after being allowed to stand at 25 °C for 30 min, it was extracted with six 70-mL portions of benzene. The combined extracts were dried by stirring with anhydrous magnesium sulfate

(22) (a) Ibne-Rasa, K. M.; Edwards, J. O. *J. Am. Chem. Soc.* **1962**, *84*, 763. (b) Ibne-Rasa, K. M.; Lauro, C. G.; Edwards, J. O. *Ibid.* **1963**, *85*, 1165.

(23) Plesničar, B. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Part C, Chapter III, pp 267–73.

(24) Ogata, Y.; Tomizawa, K.; Morikawa, T. *J. Org. Chem.* **1979**, *44*, 352.

(25) (a) Gillespie, R. J.; Malhotra, K. C. *J. Chem. Soc. A* **1967**, 1994. (b) Gillespie, R. J.; Malhotra, K. C. *Ibid.* **1968**, 1933.

(26) Ogata, Y.; Tomizawa, K.; Ikeda, T. *J. Org. Chem.* **1978**, *43*, 2417.

(27) Flürscheim, B.; Holmes, E. L. *J. Chem. Soc.* **1928**, 3041.

(28) Crockford, H. D.; Adlestone, J. A. *J. Phys. Chem.* **1936**, *40*, 303.

(29) Kaufmann, A. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 3480.

for 1 h. Filtration, followed by concentration of the filtrate to dryness under reduced pressure at 25 °C, gave 3.8 g (76%) of *N*-nitro-3,4-dinitroaniline (33) as orange yellow crystals, mp 92–96 °C (lit.^{19c} mp 94 °C). Owing to its instability, the compound was used immediately, without further purification, for rearrangement to the trinitroanilines 4 and 6 as described below.

2,3,4-Trinitroaniline (4) and 2,4,5-Trinitroaniline (6). *N*-Nitro-3,4-dinitroaniline (33; 3.8 g, 0.0167 mol) was stirred with 50 mL of concentrated H₂SO₄ at 0 °C for 1 h. The orange-brown solution was allowed to warm to ambient temperature and stand at 25 °C for 16.5 h. It was then poured onto crushed ice, and the yellow precipitate was filtered and washed thoroughly with water to yield 2.8 g (74%) of a mixture of 2,3,4-trinitroaniline (4, 40%) and 2,4,5-trinitroaniline (6, 60%) by NMR assay. The mixture was separated by chromatography on a silica gel column by elution with ether to yield a fast-moving fraction (1.7 g) which was rechromatographed to yield 1.2 g of the crude 2,4,5 isomer (88% assay), mp 180–190 °C; recrystallization from methanol gave 0.70 g of 2,4,5-trinitroaniline (6, 99% assay) as chunky, deep orange crystals: mp 192–195 °C (lit.^{19b} mp 202 °C); NMR (Me₂SO-*d*₆) δ 8.63 (s, CH at C-6), 7.30 (s, CH at C-3), 8.68 (s, NH₂).

A second, slower moving fraction was obtained in the initial column chromatography by elution with ether/methanol (9:1) which was high purity 2,3,4-trinitroaniline (total yield, 0.9 g). Recrystallization from methanol gave chunky prisms of 2,3,4-trinitroaniline (4): mp 208–210 °C (lit.^{19b} mp 210 °C); NMR (Me₂SO-*d*₆) δ 8.15, 7.17 (q, *J* = 10 Hz), 8.40 (NH₂).

1,2,3,4-Tetranitrobenzene (18). 2,3,4-Trinitroaniline (4; 0.228 g, 1 mmol) was dissolved in 11.0 mL of 100% H₂SO₄ at 10 °C. Hydrogen peroxide (1.11 mL of 98% assay, 46.0 mmol) was added with stirring during 1 min. Stirring was continued at 10–18 °C for 24 h (CaCl₂ tube attached). The reaction mixture, containing a white precipitate, was extracted with five 15-mL portions of methylene chloride. After the combined extracts were dried by being stirred with MgSO₄ for 1 h and filtered and the filtrate was concentrated to dryness, there was obtained 0.20 g (78%) of 1,2,3,4-tetranitrobenzene. mp 118–120 °C; two recrystallizations from pure chloroform gave large flat prisms, mp 120–121 °C. The sulfuric acid solution remaining after the CH₂Cl₂ extraction was poured onto ice to yield 0.044 g (19%) of recovered 2,3,4-trinitroaniline, mp 206–209 °C. The yield of 18 based on unrecovered reactant is 96%. Anal. Calcd for C₆H₂N₄O₈: C, 27.92; H, 0.78; N, 21.71; mol wt 258.11. Found: C, 28.09; H, 0.77; N, 21.62; mol wt 258 (mass spectrum M⁺).

The above procedure was employed in the oxidations of 2,4,5-trinitroaniline (6) to 1,2,4,5-tetranitrobenzene (20) and 3-amino-2,4,6-trinitrotoluene⁷⁰ to 2,3,4,6-tetranitrotoluene (21). 1,2,3-Trinitrobenzene (16) was prepared similarly from 2,6-dinitroaniline (Aldrich) except that concentrated (96%) H₂SO₄ was substituted for 100% H₂SO₄. Similar procedures were employed for the preparation of 2,2',3,3',4,4',6,6'-octanitrobiphenyl (25), 4,6-bis(2,3,4,6-tetranitrophenyl)-1,3-dinitrobenzene (26), and 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl (11),³¹ 2,4-bis(3-amino-2,4,6-trinitrophenyl)-1,5-dinitrobenzene (12),³² and 3-amino-2,2',4,4',6,6'-hexanitrostilbene (10),³² respectively, except that 1% solutions of reactant in 20% oleum solvent were treated with ca. 200 molar equiv of 90% H₂O₂ as oxidant. Results are summarized in Table I.

1,3-Difluoro-2,4,5,6-tetranitrobenzene (17). A solution containing 3.0 g (13.7 mmol) of 3,5-difluoro-2,4,6-trinitroaniline (3)³³ in 300 mL of concentrated sulfuric acid and 300 mL of 30% fuming sulfuric acid was prepared and cooled to 0 °C in an ice-salt bath. With good stirring, 34.5 mL of 90% hydrogen peroxide was added in ca. 6-mL portions, keeping the temperature below 15 °C. The solution, protected by a Drierite drying tube, was then stirred at ambient temperature for 18 h before it was extracted with three 200-mL portions of dry methylene chloride. The combined methylene chloride extracts were treated with magnesium sulfate and charcoal, filtered, and concentrated to ca. 25

mL before dry hexane was slowly added. When an appreciable amount of crystals had formed from the hot solution, it was cooled and filtered to give 2.48 g of crystals, mp 98.5–100.5 °C; by concentration of the filtrate a second crop was obtained (0.33 g, mp 97–99 °C; total yield of 17, 2.81 g, 84%). Anal. Calcd for C₆F₂N₄O₈: C, 24.50; F, 12.92; N, 19.05; mol wt 294. Found: C, 24.39; H, 0.05; F, 12.82; N, 18.89; mol wt 294 (mass spectrum, M⁺).

The above procedure was employed for the preparation of 1,5-difluoro-2,3,4-trinitrobenzene (15) by oxidation of 3,5-difluoro-2,6-dinitroaniline (1)³³ (Table I).

Pentanitrofluorobenzene (27). Pentanitrofluorobenzene is very sensitive to moisture; dry glassware must be used and moisture excluded when handling this compound. To a well-stirred solution of 120 mL of concentrated sulfuric acid and 270 mL of 30% fuming sulfuric acid at 20 °C was added 2.0 g (5.8 mmol) of 1,3-diacetamido-5-fluoro-2,4,6-trinitrobenzene 13³⁴ in small portions. The mixture was cooled in an ice-salt bath during the addition of 30 mL of 90% hydrogen peroxide in 3-mL portions. The reaction mixture, protected by a Drierite drying tube, was then kept at 0 °C for 3 h and at ambient temperature for 20 h before it was extracted with 180 mL of methylene chloride; the extract was stirred with sodium sulfate and then decanted into a round-bottomed flask. Gentle heating while a stream of dry nitrogen was passed into the flask removed the solvent to give 0.43 g (23%) of pale yellow crystalline 27, mp 147–150 °C. The solid was dissolved in warm, dry carbon tetrachloride, and the solution was treated with sodium sulfate and decanted. Cooling gave pale yellow crystals of 27, mp 152–154 °C. Anal. Calcd for C₆FN₅O₁₆: C, 22.44; F, 5.92; N, 21.81; mol wt 321. Found: C, 22.67; H, <0.05; F, 6.11; N, 21.94; mol wt 321 (mass spectrum, M⁺).

3,5-Diacetamido-2,4,6-trinitrotoluene. A solution of 3,5-diamino-2,4,6-trinitrotoluene³⁵ (0.514 g, 2.0 mmol) in 5 mL of pyridine containing acetic anhydride (0.45 g, 4.4 mmol) was heated under reflux for 0.5 h. The cooled solution was poured into water and the product filtered to yield 0.41 g (60%) of 3,5-diacetamido-2,4,6-trinitrotoluene: mp 325–326 °C after recrystallization from acetonitrile; NMR (CD₂Cl₂ and 5% (CD₃)₂SO) δ 2.32 (s, CH₃C, 3), 2.05 (s, CH₃CO, 6). Anal. Calcd for C₁₁H₁₁N₅O₈: C, 38.71; H, 3.25; N, 20.53. Found: C, 38.82; H, 3.27; N, 20.51.

3,5-Bis(diacetylamino)-2,4,6-trinitrotoluene (14). A solution of 3,5-diamino-2,4,6-trinitrotoluene³⁵ (2.0 g, 7.78 mmol) in acetic anhydride (200 mL) containing 0.5 mL of concentrated H₂SO₄ was heated under reflux for 2 h. The cooled solution was poured into 1 L of cold water and stirred until a brown precipitate was produced. The product was filtered, washed thoroughly with water, and dried to yield 2.3 g (70%) of 14: mp 151–153 °C after recrystallization from ethanol; NMR (CD₂Cl₂) δ 2.38 (s, CH₃CO, 12), 2.44 (s, CH₃, C, 3). Anal. Calcd for C₁₅H₁₅N₅O₁₆: C, 42.36; H, 3.55; N, 16.47. Found: C, 41.23; H, 3.53; N, 17.45. On being allowed to stand at ambient temperature for several weeks, the compound is slowly converted to 3,5-diacetamido-2,4,6-trinitrotoluene, mp 325–326 °C.

Pentanitrotoluene (28). To a solution of freshly prepared, unrecrystallized 3,5-bis(diacetylamino)-2,4,6-trinitrotoluene (14; 1.0 g, 2.35 mmol) in 50 mL of 30% oleum was added dropwise, at a constant rate during 4.5 h, 4.0 mL of 90% hydrogen peroxide, keeping the temperature at 20–25 °C. After being stirred for 18 h at 25 °C, the entire reaction mixture (containing some yellow solid which was difficult to separate by filtration) was extracted thoroughly with methylene chloride. After the extracts were dried by being stirred with magnesium sulfate for 2 h and filtered and the filtrate was concentrated to dryness, there was obtained 0.8 g of pale yellow solid which was recrystallized from pure dry chloroform to yield 0.4 g (54%) of 28, mp 225–240 °C. Use of 3,5-diacetamido-2,4,6-trinitrotoluene in the above procedure gave only a trace of 28. Anal. Calcd for C₇H₃N₅O₁₆: C, 26.51; H, 0.95; N, 22.08. Found: C, 26.50; H, 0.93; N, 21.87.

Hexanitrobenzene (23). Procedure B.³⁶ Pentanitroaniline (9; 0.50 g, 1.57 mmol) was dissolved in 50 mL of trifluoro-

(30) Jorgenson, M. J.; Hartter, D. R. *J. Am. Chem. Soc.* **1963**, *85*, 878.

(31) Kamlet, M. J.; Sickman, D. V. U.S. Patent 3 320 320, May 16, 1967; *Chem. Abstr.* **1968**, *68*, P59264.

(32) Lerom, M. W.; Peters, H. M.; Ross, D. L.; Hill, M. E. *J. Chem. Eng. Data* **1974**, *19*, 389.

(33) Sitzmann, M. *J. Org. Chem.*, **1978**, *43*, 1241.

(34) The preparation of this compound is described in a forthcoming publication of M. E. Sitzmann.

(35) (a) Palmer, A. W. *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 3501. (b) Joshi, S. S.; Gupta, S. P., *J. Indian Chem. Soc.* **1959**, *36*, 329.

(36) Procedure A appears in ref 4.

methanesulfonic acid by heating to 70 °C. After the mixture cooled to 50 °C, 2.50 mL of 90% H₂O₂ was added during 15 min (ice bath cooling to maintain the temperature at 45–55 °C). During the addition, the color of the solution changed from orange to green and then to yellow. After the solution was stirred at ambient temperature for 19 h, it was extracted with two 60-mL portions of methylene chloride. The combined extracts were stirred with 15 g of MgSO₄ for 5 h to remove trifluoromethanesulfonic acid. After filtration, the filtrate was concentrated to dryness under reduced pressure, leaving 0.55 g of pale yellow solid which was crystallized from 6.0 mL of pure, dry chloroform to yield 0.49 g (90%) of hexanitrobenzene (23), mp 24–262 °C (phase transition at 115 °C), identical with an authentic sample.⁴

Hexanitrobenzene (23). Procedure C.³⁶ Pentanitroaniline (9; 1.0 g, 3.14 mmol) was dissolved in 80 mL of trifluoromethanesulfonic acid by heating to 70 °C. The mixture was cooled to 24 °C, 2.60 g (9.62 mmol) of potassium persulfate was added in one portion, and the resulting solution was stirred at ambient temperature for 18 h. After extraction with two 75-mL portions of methylene chloride, the combined extracts were stirred with 20 g of MgSO₄ for 6 h to remove trifluoromethanesulfonic acid. After filtration, the solvent was removed from the filtrate under reduced pressure, leaving 0.63 g of a yellow solid. This material, a mixture of pentanitroaniline and hexanitrobenzene, was stirred with CCl₄ for 19 h and filtered; removal of solvent from the filtrate gave 0.23 g (21%) of hexanitrobenzene, mp 239–258 °C.

Treatment of pentanitroaniline with potassium persulfate in sulfuric acid gave recovered pentanitroaniline only. To pentanitroaniline (9; 1.0 g, 3.14 mmol) in 50 mL of 20% oleum was

added 6.5 g of potassium persulfate, and the mixture was stirred at 25 °C for 24 h. The mixture was extracted three times with methylene chloride. After being dried with MgSO₄, the combined extracts were concentrated to dryness to yield 0.53 g of crude pentanitroaniline as yellow crystals; trituration of this product with pure chloroform gave 0.40 g of recovered pentanitroaniline, mp 193–199 °C. The sulfuric acid solution remaining when poured onto ice gave a trace of orange solid. No hexanitrobenzene could be isolated from the reaction products.

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Registry No. 1, 64884-81-7; 2, 606-22-4; 3, 73333-89-8; 4, 73333-90-1; 5, 489-98-5; 6, 32650-52-5; 7, 22603-58-3; 8, 3698-54-2; 9, 21985-87-5; 10, 51168-33-3; 11, 17215-44-0; 12, 53517-46-7; 13, 73333-91-2; 14, 73333-92-3; 15, 73333-93-4; 16, 603-13-4; 17, 73333-94-5; 18, 73333-95-6; 19, 3698-53-1; 20, 5967-26-0; 21, 73333-96-7; 22, 68630-38-6; 23, 13232-74-1; 24, 73347-63-4; 25, 73333-97-8; 26, 73333-98-9; 27, 73333-99-0; 28, 73334-00-6; 29, 122-28-1; 30, 60956-27-6; 31, 73334-01-7; 32, 610-41-3; 33, 73334-02-8; 3,5-dinitroaniline, 618-87-1; 3,5-diacetamido-2,4,6-trinitrotoluene, 73334-03-9; 3,5-diamino-2,4,6-trinitrotoluene, 73334-04-0; peroxydisulfuric acid, 13445-49-3.

Alkali Metal *O,O*-Diethyl Phosphorotelluroates, a Reagent Class for Deoxygenation of Epoxides, Especially Terminal Epoxides

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Epoxides are deoxygenated to olefins by alkali metal *O,O*-diethyl phosphorotelluroates. These reagents can be used in stoichiometric quantities or they can be generated continuously in situ from tellurium under conditions that approach a catalytic nature with respect to the metal. Terminal epoxides are deoxygenated most readily, but the reaction does work for other types. In the case of epoxides formally derived from acyclic olefins, the *Z* compound reacts more easily than the *E* isomer and the deoxygenation is stereospecific. 1,2-Epoxyhexanes react faster than 1,2-epoxycyclopentanes. Selective deoxygenations, especially those in favor of terminal epoxides, are possible.

Introduction

While a large number of well-established synthetic methods depend on special properties of organic sulfur compounds,¹ the utility of selenium-based procedures was recognized only in the recent past. This area is being studied, however, in a very intensive manner, and one of its characteristic features is the rapidity with which the new selenium reactions have been accepted into the repertoire of standard methodology.² In contrast, the relevance of tellurium chemistry to synthesis is very largely

undefined. The *organic* chemistry of the metal is described in a substantial primary literature, and extremely detailed reviews are available.³ However, this large and active subject has made little contribution to synthesis by way of providing organic compounds that function as reagents. Species of the type ArTe_xAr' (*x* = 1 or 2) can be used to convert vicinal dibromides into olefins,⁴ and certain telluronium salts have been examined⁵ as catalysts for ox-

(1) Trost, B. M.; Melvin, L. S., Jr. "Sulfur Ylides—Emerging Synthetic Intermediates"; Academic Press: New York, 1975. Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978.

(2) Clive, D. L. J. *Tetrahedron* 1978, 1049; *Aldrichimica Acta* 1978, 11, 43. Sharpless, K. B.; Gordon, K. M.; Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* 1975, 8A, 9. Reich, H. J. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Part C, Chapter 1. *Acc. Chem. Res.* 1979, 12, 22.

(3) Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach: New York, 1974. Irgolic, K. J. *J. Organomet. Chem.* 1978, 158, 267. Zingaro, R. A.; Irgolic, K. In "Tellurium"; Copper, W. C., Ed.; Van Nostrand-Reinhold: New York, 1971. Petragani, N.; De Moura Campos, M. *Organomet. Chem. Rev.* 1967, 2, 61. Petragani, N. *Ann. N.Y. Acad. Sci.* 1972, 192, 10; Houben-Weyl, "Methoden der Organischen Chemie"; Georg Thieme Verlag: Stuttgart, 1955; Chapter IX, 917.

(4) De Moura Campos, M.; Petragani, N.; Thomé, C. *Tetrahedron Lett.* 1960, No. 15, 5. De Moura Campos, M.; Petragani, N. *Chem. Ber.* 1961, 94, 1759.

(5) Ohkubo, K.; Kanaeda, H. *Bull. Chem. Soc. Jpn.* 1972, 45, 11. Fukui, K.; Ohkubo, K.; Yamabe, T. *Ibid.* 1969, 42, 312.