Synthesis of Polynitrodiazophenols

Ronald L. Atkins

Chemistry Division, Research Department, Naval Weapons Center, China Lake, California 93555

William S. Wilson*†

Materials Research Laboratory, Ascot Vale, Victoria 3032, Australia

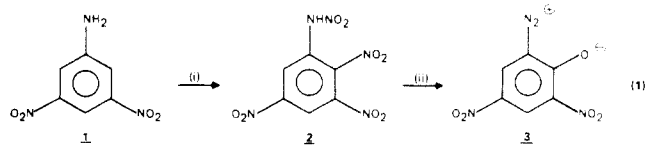
Received October 7, 1985

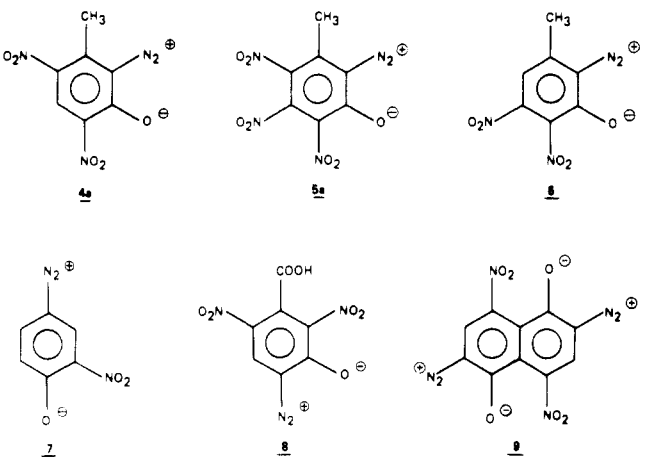
The formation of diazophenols by nitration of suitably substituted anilines and rearrangement of the nitroaromatic nitramines so formed is presented. The scope of the reaction is discussed, and a mechanism for the nitramine/diazophenol rearrangement is proposed which is consistent with ^{15}N-labeling experiments.

Polynitroanilines form a class of compounds which have been prepared in these laboratories by mixed acid nitration of suitably substituted anilines and converted to polynitroaromatics by oxidation of the amine group using peroxydisulfuric acid. This reaction sequence is exemplified by the recent synthesis of hexanitrobenzene from 3,5-dinitroaniline.[1,2]

Mixed acid nitration of anilines frequently involves reaction at the amine functionality to yield aromatic nitramines which may be cleaved in high yield to the corresponding aniline by treatment with anisole in sulfuric acid. Occasionally, this cleavage occurs even in the absence of anisole, and the nitramine does not survive the conditions of nitration. Alternatively, the nitramine may undergo "aromatic nitramine rearrangement" either under normal nitration conditions or in 96% sulfuric acid. In this rearrangement, first studied by Bamberger, the *N*-nitro group migrates to an ortho or para position on the aromatic ring.[3] This pathway has occasionally been implicated in mixed acid nitration of anilines.[4]

In addition to the products expected from nitration of anilines, from oxidation of nitroanilines, and from aromatic nitramine rearrangement, very sensitive byproducts have occasionally been isolated.[4,5] These byproducts are frequently highly colored, at least in an unpurified form. They show no exchangeable protons in the NMR spectra and show neither amine nor nitramine absorptions in the infrared. Instead they show strong absorptions at about 2200 and 1630 cm^{-1} in addition to the expected nitro group absorptions and have been identified as diazo oxides, diazophenols, or more properly, diazonium phenolates.[4-6] Although other structures may be postulated, these compounds are believed to be zwitterions, with positive and negative charges predominantly localized on the diazo and oxo groups.[7] All explode in a crude hammer/anvil impact test and decompose with various degrees of violence on heating in a capillary tube. In view of this sensitive character, these materials have until now been regarded as undesirable contaminants to be avoided wherever possible. Diazophenols prepared in this manner include 2-diazo-4,6-dinitrophenol (**3**) (DDNP or DINOL), a primary explosive conventionally prepared by diazotization of picramic acid[8] but also isolated by Scilly on thermolysis of the nitramine **2** obtained by controlled nitration of **1**[4] (eq 1), 2-diazo-3-methyl-4,6-dinitrophenol (**4a**),[9] 2-diazo-3-methyl-4,5,6-trinitrophenol (**5a**),[9] 2-diazo-3-methyl-5,6-dinitrophenol (**6**) previously assigned the structure **4a**,[5] 4-diazo-2-nitrophenol (**7**),[10] the carboxylic acid **8**,[11] and the naphthalene derivative **9**.[12]





A series of diazophenols was required for screening as explosive components of percussion- and stab-sensitive primary explosive compositions in an attempt to correlate sensitivity with chemical structure.[13] The approach initially taken to their synthesis was the conventional diazotization of the corresponding aminophenol.[8] However, the synthesis of these precursors is itself a nontrivial process and usually involves selective reduction of nitrophenols using sodium sulfide—a reaction which proved inappropriate for the more highly substituted nitrophenols. It seemed that the rearrangement of polynitroaromatic nitramines to diazophenols might be more general and might afford a useful alternative route to these compounds.

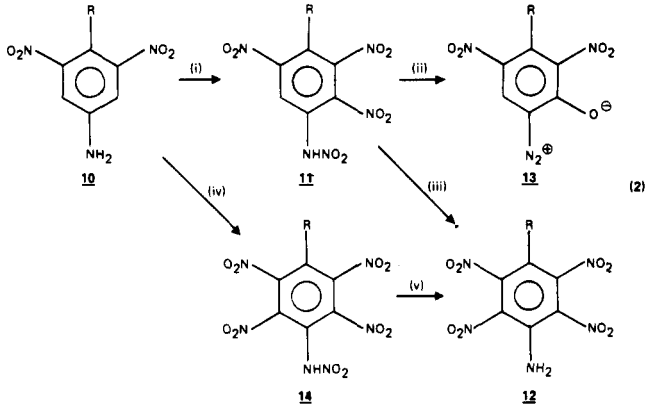
† Present address: Chemistry Division, Research Department, Naval Weapons Center, China Lake, CA 93555.

(1) (a) Nielsen, A. T.; Atkins, R. L.; Norris, W. P. *J. Org. Chem.* **1979**, *44*, 1181. (b) Nielsen, A. T.; Atkins, R. L.; Norris, W. P.; Coon, C. L.; Sitzman, M. E. *J. Org. Chem.* **1980**, *45*, 2341.
(2) Atkins, R. L.; Nielsen, A. T.; Bergens, C.; Wilson, W. S. *J. Org. Chem.* **1984**, *49*, 503.
(3) Bamberger, E.; Landsteiner, K. *Chem. Ber.* **1893**, *26*, 485.
(4) Mudge, P. R.; Salter, D. A.; Scilly, N. R. *J. Chem. Soc., Chem. Commun.* **1975**, 509.
(5) Nielsen, A. T.; Henry, R. A.; Norris, W. P.; Atkins, R. L.; Moore, D. W.; Lepie, A. H.; Coon, C. L.; Spanggord, R. J.; Son, D. V. H. *J. Org. Chem.* **1979**, *44*, 2499.
(6) Glowiak, B. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1960**, *8*, 1.
(7) (a) Kazitsyna, L. A.; Klyueva, N. D. *Izv. Akad. Nauk. SSSR, Ser Khim.* **1970**, *1*, 192. (b) Milliaresi, E. E.; Ruchkin, V. E.; Buchneva, L. M.; Ruchkina, N. G.; Kazitsyna, L. A. *Vestn. Mosk. Univ. Ser 2: Khim.* **1979**, *20*, 465 and others.
(8) Greiss, G. *Ann.* **1858**, *106*, 123.
(9) Atkins, R. L.; Hollins, R. A.; Nielsen, A. T.; Norris, W. P.; Wilson, W. S. U.S. Patent 4 451 681, May 29, 1984. Atkins, R. L.; Hollins, R. A.; Wilson, W. S., submitted for publication in *J. Org. Chem.*
(10) Vaughn, J.; Phillips, L. *J. Chem. Soc.* **1947**, 1560.
(11) Chafin, A.; Nielsen, A. T., to be published.
(12) Nielsen, A. T.; DeFusco, A. A.; Browne, T. E. *J. Org. Chem.* **1985**, *50*, 4211.
(13) Spear, R. J.; Wilson, W. S.; Redman, L. D. *Combust. Flame* **1985**, *60*, 89.

This proved to be the case, and this paper discusses the scope of the reaction and the mechanism by which it occurs.

Results and Discussion

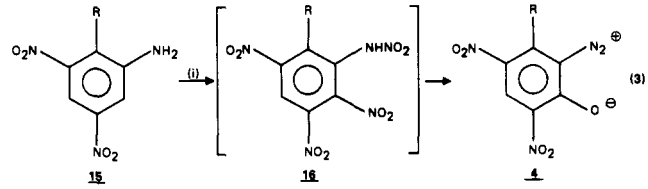
4-Amino-2,3,5,6-tetranitrotoluene (**12a**) was synthesized from 4-amino-2,6-dinitrotoluene (**10a**) (eq 2). Nitration of **10a** using nitric acid in acetic and sulfuric acids at 0 °C gave the nitramine **11a**, which rearranges to the desired tetranitro product **12a** on stirring in sulfuric acid at room temperature. (An improved route involved nitration of



(i) 90% HNO_3, 96% H_2SO_4, AcOH, 0°C
(ii) CH_2Cl_2, REFLUX
(iii) 96% H_2SO_4
(iv) 90% HNO_3, 96% H_2SO_4, 0°C
(v) ϕ OMe, 96% H_2SO_4, RT

a R = CH_3
b R = Cl

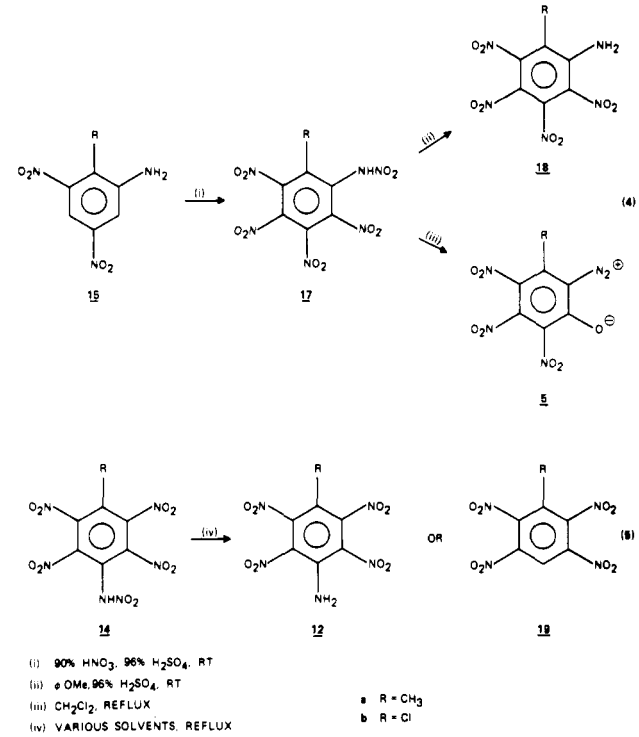
10a in sulfuric acid to give the nitramine **14a**, which may be cleaved to **12a** by using anisole in sulfuric acid.[9]) However, when heated in dichloromethane under reflux, **11a** underwent facile rearrangement to the diazophenol **13a**. This compound has also been prepared by diazotization of 2-amino-5-methyl-4,6-dinitrophenol.[14] When a similar procedure was followed with 2-amino-4,6-dinitrotoluene (**15a**), namely, nitration with nitric acid in a mixture of acetic and sulfuric acids at 0 °C, the diazophenol **4a** was obtained directly and in good yield without the (presumed) intermediate nitramine **16a** being isolated (eq 3).



(i) 90% HNO_3, 96% H_2SO_4, AcOH, 0°C

a R = CH_3
b R = Cl

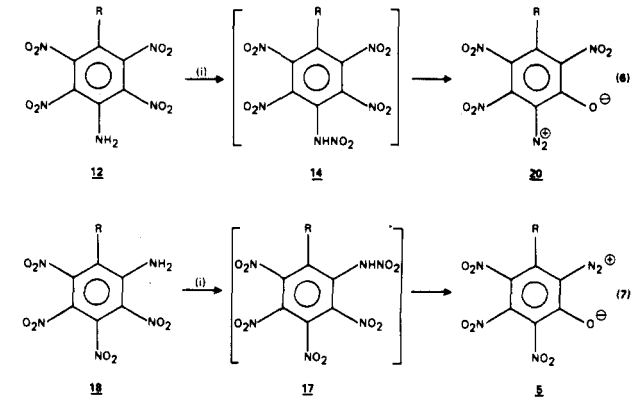
2-Amino-3,4,5,6-tetranitrotoluene (**18a**) is conveniently prepared by nitration of **15a** in 80% sulfuric acid, followed by cleavage of the resultant nitramine **17a** using anisole in sulfuric acid.[9] As indicated earlier, the nitramine is also subject to rearrangement to the diazophenol **5a** on heating in dichloromethane under reflux (eq 4). By way of comparison, however, the isomeric **14a** obtained on nitration of **10a** proved unexpectedly stable to such thermal rearrangement. Reflux in dichloromethane gave no reaction, while prolonged reflux in chloroform, carbon tetrachloride, or acetone resulted in cleavage of the nitramine group to give 4-amino-2,3,5,6-tetranitrotoluene (**12a**). Reflux in ethyl acetate solution resulted in elimination of the entire nitramine function to give 2,3,5,6-tetranitrotoluene (**19a**) with no trace of diazophenol being detected (eq 5). This constitutes the first reported synthesis of **19a**.



(i) 90% HNO_3, 96% H_2SO_4, RT
(ii) ϕ OMe, 96% H_2SO_4, RT
(iii) CH_2Cl_2, REFLUX
(iv) VARIOUS SOLVENTS, REFLUX

a R = CH_3
b R = Cl

The diazophenol **20a** was ultimately prepared by the action of nitric acid and acetic anhydride on amine **12a** in acetic acid solution. The nitramine **14a** was neither isolated nor detected in the reaction mixture, but was presumed to be an intermediate (eq 6). Subsequently, the diazophenol **5a** was also prepared by nitration of the corresponding amine **18a** under the same conditions, again without the the isolation of the intermediate nitramine **17a** (eq 7).

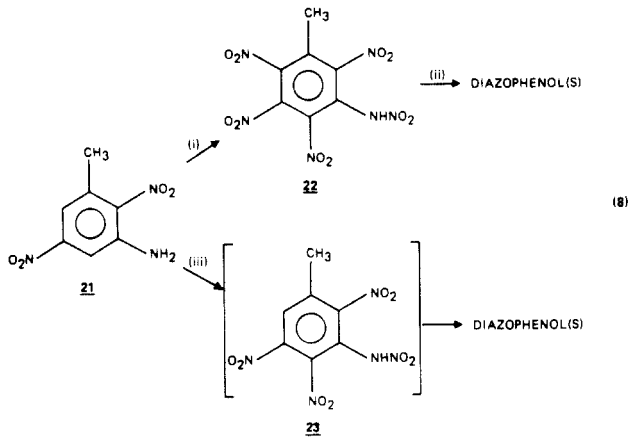


(i) 100% HNO_3, Ac_2O, AcOH, 0°C

a R = CH_3
b R = Cl

The same procedures were employed in an attempt to prepare diazophenols from 3-amino-2,5-dinitrotoluene (**21**) (eq 8). Nitration in 96% sulfuric acid gave the nitramine **22**, which yielded a red oil when heated in dichloromethane. This product appeared to be essentially a single compound, showing only a single methyl signal in the NMR and also showed typical diazophenol absorptions at ca. 2200 and 1630 cm^{-1} in the infrared spectrum. However, attempts at crystallization and purification proved unsuccessful, and the structure of the product could not be elucidated. Nitration in a mixture of acetic and sulfuric acid also gave a red oil, which also appeared to be essentially a single compound with one major methyl signal and one aromatic proton in the NMR but a double diazo peak

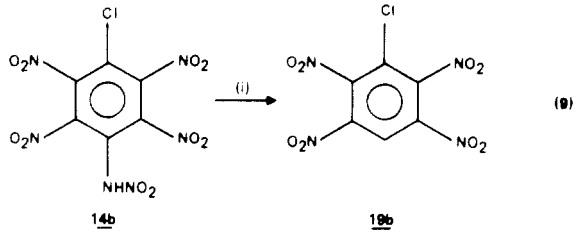
(14) Spear, R. J., unpublished results.



(i) 90% HNO_3, 96% H_2SO_4, 0°C
(ii) CH_2Cl_2, REFLUX
(iii) HNO_3, 96% H_2SO_4, AcOH, 0°C

at 2200 cm^{-1} in the infrared. Again, attempts at recrystallization and purification were fruitless, and the precise structure remains uncertain. However, the product is probably one of the diazophenols derived from the nitramine **23**.

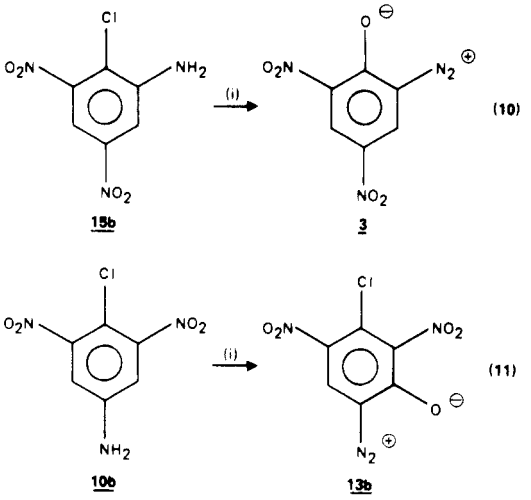
4-Chloro-2,3,5,6-tetranitroaniline (**12b**) may be prepared by nitration of 4-chloro-3,5-dinitroaniline (**10b**) in 96% sulfuric acid and cleavage of the resultant nitramine **14b** using anisole in 96% sulfuric acid[9] (eq 2). Nitration of **12b** using nitric acid and acetic anhydride in acetic acid gave the diazophenol **20b** (eq 6). It was believed that the nitramine **14b** was an intermediate in the formation of the diazophenol. However, **14b** was unchanged after heating for several days in dichloromethane under reflux. Further, treatment of **14b** with nitric acid and acetic anhydride in acetic acid gave 3-chloro-1,2,4,5-tetranitrobenzene (**19b**) rather than the expected diazophenol **20b** (eq 9). Nitration of 4-chloro-3,5-dinitroaniline (**10b**) in acetic acid and sulfuric acid gave the diazophenol **13b**. Once again, the nitramine **11b** was presumed to be an intermediate but was not isolated (eq 2).



(i) 90% HNO_3, Ac_2O, AcOH, RT

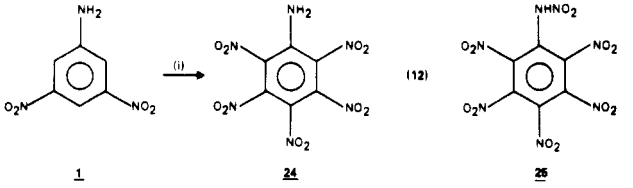
In a similar fashion, nitration of the isomeric 2-chloro-3,5-dinitroaniline (**15b**) using nitric acid in acetic and sulfuric acid gave the diazophenol **4b**; again, the presumed intermediate nitramine **16b** was not isolated (eq 3). Nitration of **15b** using nitric acid in 80% sulfuric acid also gave **4b**, but when the reaction was carried out in 96% sulfuric acid, the predominant product was the nitramine **17b**, with a smaller quantity of **4b** also being isolated. Cleavage of the nitramine **17b** by stirring with anisole in 96% sulfuric acid at ambient temperature overnight (or by prolonged stirring in 96% sulfuric acid alone) gave 2-chloro-3,4,5,6-tetranitroaniline (**18b**). This amine yielded the diazophenol **5b** on treatment with nitric acid and acetic anhydride in acetic acid. Diazophenol **5b** can also be prepared by thermolysis of the nitramine **17b** in dichloromethane (eq 4). The relative stability of **14b** compared with the isomeric **17b** exactly parallels the behavior of the analogous toluene derivatives **14a** and **17a**.

Interestingly, nitration of **15b** using 100% nitric acid in 20% oleum gave 2-diazo-4,6-dinitrophenol (**3**), the chloro group having been displaced in the reaction (eq 10). In contrast, nitration of **10b** under the same conditions gave 3-chloro-2-diazo-4,6-dinitrophenol (**13b**) (eq 11).



(i) 100% HNO_3, 20% oleum, 0°C

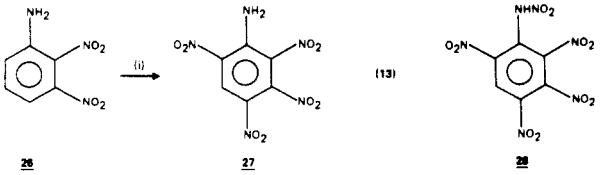
These procedures of nitration and thermolysis do not lead invariably to diazophenols, however. The nitration of 3,5-dinitroaniline (**1**) under relatively mild conditions (70% nitric acid in 96% sulfuric acid) to give *N*,2,3,5-tetranitroaniline (**2**) and subsequently 2-diazo-4,6-dinitrophenol (**3**) has been discussed above (eq 1). Nitration under more forcing conditions (100% nitric acid in 100% sulfuric acid at 70 °C) gave only 2,3,4,5,6-pentanitroaniline (**24**) (eq 12). There were indications that *N*,2,3,4,5,6-



(i) 100% HNO_3, 100% H_2SO_4, 70°C

hexanitroaniline (**25**) might be involved as a transient intermediate, but no trace of nitramine or diazophenol could be isolated either from this reaction, from nitration under still more forcing conditions (100% nitric acid in 20% oleum), or from treatment of pentanitroaniline (**24**) with nitric acid and acetic anhydride in acetic acid solution. The latter reactions resulted only in general decomposition of the polynitroaromatic.

Similarly, nitration of 2,3-dinitroaniline (**26**) using 70% nitric acid in 96% sulfuric acid afforded 2,3,4,6-tetranitroaniline (**27**) with no evidence of the presumed intermediate nitramine **28** or any diazophenol which might be derived from it (eq 13). Nitration under milder conditions (80% sulfuric and acetic acid) gave complex mixtures which appeared to contain diazophenols but which proved to be intractable. The instability of the nitramines **25** and

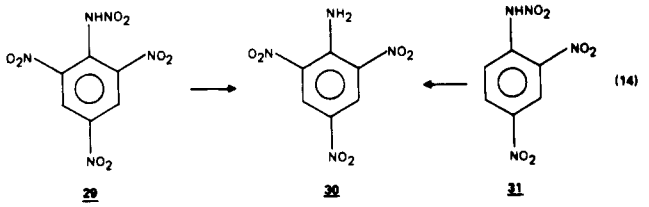


(i) 70% HNO_3, 96% H_2SO_4, 0°C

28 with respect to cleavage under the conditions of ni-

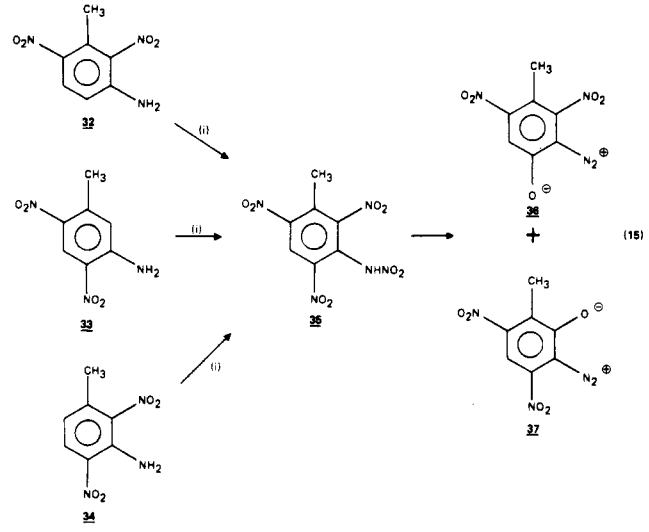
tration could be explained on electronic or (better) steric grounds but should be contrasted with the comparative stability of the highly substituted nitramines **14a,b**, **17a,b**, and **22**, all of which were readily isolated and characterized.

On the other hand, heating *N*,2,4,6-tetranitroaniline (**29**) in a variety of solvents resulted only in nitramine cleavage to give 2,4,6-trinitroaniline (picramide) (**30**), while *N*,2,4-trinitroaniline (**31**) underwent nitramine rearrangement to the same product (eq 14); in neither case was any trace of diazophenol detected.



(14)

In every example up until now in which a polynitroaromatic nitramine has undergone rearrangement to give a diazophenol, there has been an electron-withdrawing nitro group ortho to the nitro group displaced (and meta to the nitramine function). Further, those nitramines examined which did *not* contain this feature, namely, **29** and **31**, did not undergo the rearrangement. It appeared, therefore, that the presence of the two adjacent nitro groups was an essential prerequisite. However, nitration of 3-amino-2,6-dinitrotoluene (**32**), 3-amino-4,6-dinitrotoluene (**33**), and 3-amino-2,4-dinitrotoluene (**34**) using 90% nitric acid in 96% sulfuric acid gave in each case essentially the same 4:1 mixture of products. The major component was isolated with some difficulty and identified on the basis of IR and NMR spectra as the diazophenol **36**; the minor product has not yet been isolated but could be either the isomeric diazophenol **37** or the common precursor, the nitramine **35** (eq 15). This is the first example encountered of diazophenol formation from a nitramine precursor which does *not* contain two vicinal nitro groups on the aromatic ring.



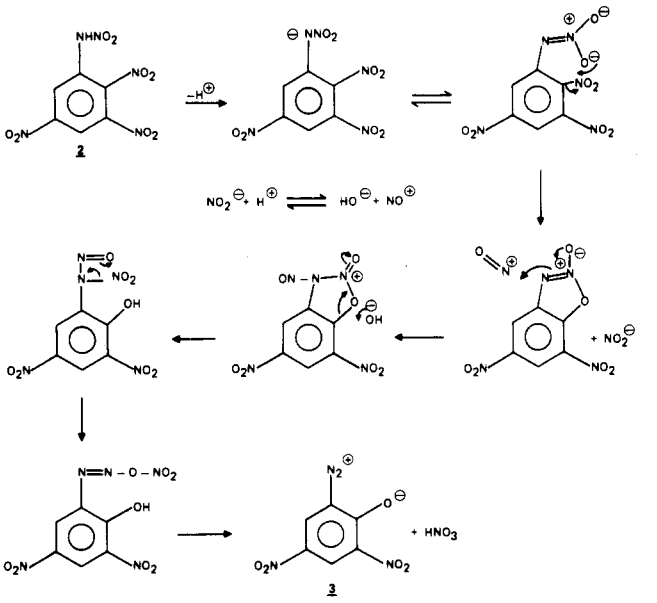
(15)

(i) 90% HNO_3, 96% H_2SO_4, RT

Mechanism

The rearrangement of nitroaromatic nitramines to diazophenols involves a formal elimination of the elements of nitric acid. The mechanism by which this elimination occurs is far from obvious. In the majority of examples, the nitramine contains a nitro group ortho to that displaced, activating that site to electrophilic aromatic substitution, and meta to the nitramine functionality. Molecules which do not have this structural feature appear not to be subject to nitramine/diazophenol rearrangement. The formation of **36** on nitration of the isomeric **32–34** is anomalous in this regard. An intramolecular electrocyclic rearrangement seems attractive in most cases but cannot easily be invoked in the formation of 4-diazo-2-nitrophenol (**7**). This reaction presumably involves intermolecular rearrangement or solvent cage participation.

Scheme I



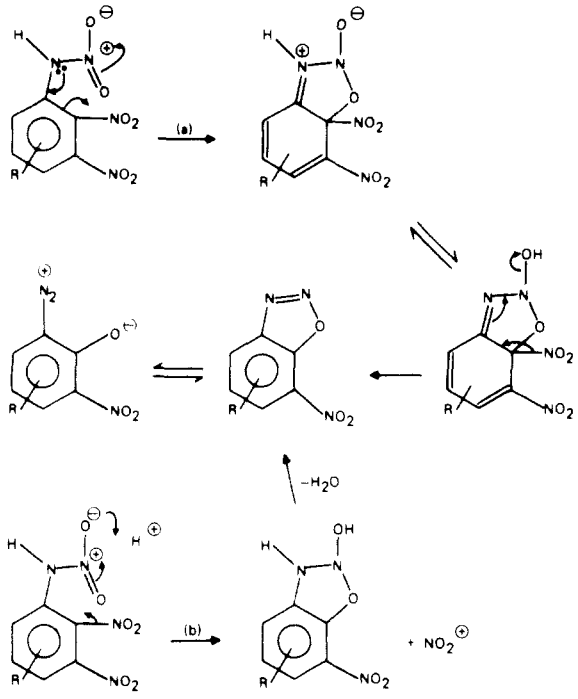
Scilly reported the formation of 2-diazo-4,6-dinitrophenol (**3**) from *N*,2,3,5-tetranitroaniline (**2**) via intramolecular nucleophilic displacement of the 2-nitro group and proposed the mechanism presented in Scheme I.[4] Several features of Scilly's reaction pathway are debatable, including abstraction of the nitramine proton under these reaction conditions and elimination of the nitro group as a nitrite ion. A more plausible electrocyclic rearrangement is presented by pathway a in Scheme II and involves electrophilic attack by the nitramine oxygen at the ortho position and proton migration, followed by elimination of nitronium and hydroxide ions. A minor variation (b) on this mechanism would also account for the rearrangement under acid conditions.

Another possible mechanism (Scheme III) involves rearrangement to a nitrito function of the nitro group adjacent to the nitramine and then displacement of the *N*-nitro group. The nitro–nitrito rearrangement has been observed in photolysis[15] and electron impact[16] of nitroaromatics and has been invoked to account for the chemical reactivity and explosive sensitiveness of vicinal trinitroaromatics.[17]

A series of ^{15}N-labeling experiments was performed to identify the fate of the nitrogen atoms in the nitramine–diazophenol rearrangement. The formation of 2-diazo-3-methyl-4,5,6-trinitrophenol (**5a**) was selected as the reaction to be investigated. Diazophenol **5a** results from nitration of 2-amino-3,4,5,6-tetranitrotoluene (**18a**) in acetic acid/acetic anhydride (eq 7) or by thermolysis of 2-amino-*N*,3,4,5,6-pentanitrotoluene (**17a**) in dichloromethane (eq 4). Nitration of 2-amino-4,6-dinitrotoluene

(15) Hunt, R.; Reid, S. T. *J. Chem. Soc., Perkins Trans. 1* **1972**, 2527.
(16) Beyman, J. H.; Saunders, R. A.; Williams, A. E. *Ind. Chim. Belg.* **1964**, *4*, 311.
(17) Dewar, M. J. S.; Ritchie, J. P.; Alster, J. *J. Org. Chem.* **1985**, *50*, 1031.

Scheme II



Scheme III

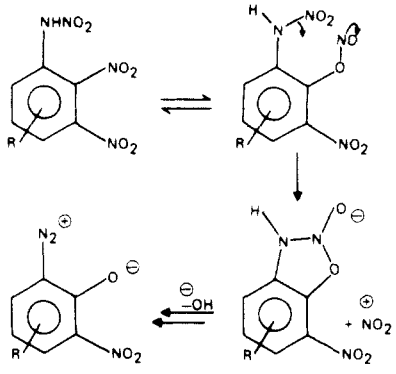


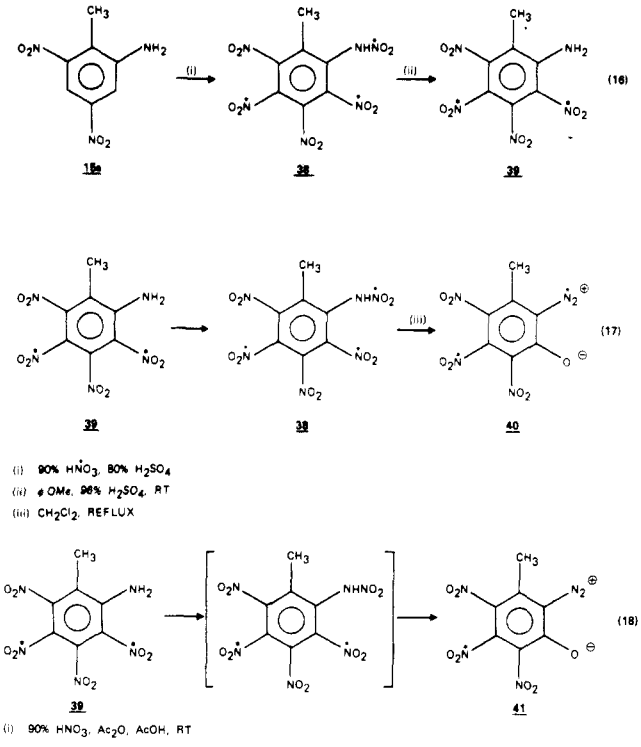
Table I. Normalized Parent Ion Distribution for ^{15}N-Labeled 2-Diazo-3-methyl-4,5,6-trinitrophenols

	m/e			
compd	269	270	271	272
5a[a]	88	10	2	
40	44	42	13	1
41	61	34	4	1
42	63	31	4	1

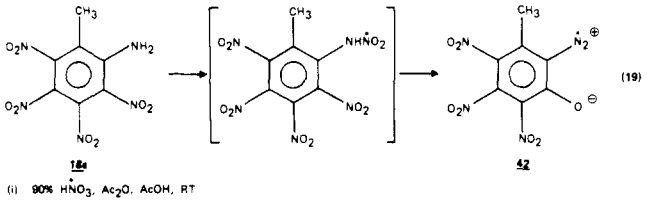
[a] Unlabeled.

(**15a**) with ^{15}N-labeled nitric acid (ca. 30% ^{15}N) gave the triply labeled nitramine **38**, which was cleaved by treatment with anisole in sulfuric acid to the doubly labeled amine **39** (eq 16). Thermolysis of **38** or nitration of **39** with labeled nitric acid gave the doubly labeled diazophenol **40** (eq 17), which was characterized by the emergence of a second diazo peak at 2170 cm^{-1}, by broadening of the nitro absorptions in the infrared spectrum, and by the expected isotope distribution for the parent ion in the mass spectrum (see Table I).

On the other hand, nitration of **39** with unlabeled nitric acid gave **41** labeled only at the nitro group (eq 18), characterized by a single diazo absorption but broadened nitro absorptions in the infrared spectrum and by the expected isotope ratio for the parent ion in the mass spectrum (see Table I).



Nitration of unlabeled amine **18a** with ^{15}N-labeled nitric acid gave **42** labeled only at the diazo function (eq 19) and characterized by the additional diazo absorption at 2170 cm^{-1} but no broadening of the nitro absorption in the infrared spectrum and by the expected isotope ratio for the parent ion in the mass spectrum.



These labeling studies demonstrate that the two nitramine nitrogens are retained in the diazo group of the diazophenol, while the nitrogen atom of the adjacent nitro group is eliminated completely from the molecule. The source of the phenolic oxygen has yet to be established, but might best be achieved by means of an analogous ^{18}O-labeling study. It is apparent, however, that the mechanism does *not* involve displacement and loss of the *N*-nitro group in a sequence such as Scilly's mechanism (Scheme I) or that illustrated in Scheme III. Rather, the data are fully consistent with the mechanism presented in Scheme II.

The rearrangement of *N*,2,3-trinitroanilines to diazophenols appears, then, to be quite general and offers a new and useful route to this class of compounds. It is proposed that the rearrangement proceeds via an electrocyclic displacement by the nitramine oxygen of the 2-nitro group, which is activated to electrophilic displacement. Such a mechanism is consistent with the available data.

Experimental Section

WARNING: Polynitroaromatics are powerful explosives, while diazophenols are sensitive to friction, heat, and impact, and all should be handled with extreme caution. Satisfactory elemental analyses were obtained for new compounds, each of which showed the expected parent ion as a prominent signal in the mass spectrum; all previously known compounds were spectrally identical with authentic materials prepared by established procedures. Melting points were determined in capillary tubes by

using a Buchi 510 melting point apparatus or by using a Leitz Ortholux microscope with an attached Mettler FLP-2 hot stage. Infrared spectra were recorded as potassium bromide disks with a Perkin-Elmer 137 or 683 spectrophotometer. Proton magnetic resonance spectra were recorded with a Varian EM-360 or EM-360L NMR spectrometer, by using samples of 2–5% concentration in acetone-d_6 with tetramethylsilane as an internal standard. Mass spectra were recorded on a vacuum generator VG 7035 double-focusing 70-eV instrument.

2-Amino-4,6-dinitrotoluene (15a) was prepared by reduction of 2,4,6-trinitrotoluene (TNT) using iron powder in acetic acid.[18] Under an atmosphere of dry nitrogen, TNT (4.0 g, 17.6 mmol) was dissolved in glacial acetic acid (88 mL). Iron powder (400 mesh, 4 × 0.82 g, 58.6 mmol) was added over 2 h with mechanical stirring. The reaction mixture was filtered and diluted to 160 mL with distilled water. The flocculant yellow precipitate was filtered and dried at the pump to give 2.67 g (77%) containing 10% 4-amino-2,6-dinitrotoluene (**10a**) by NMR. Recrystallization from ethanol gave pure **15a** (1.33 g, mp 175–177 °C) with IR and NMR spectra identical with those of authentic material.

2-Chloro-3,5-dinitroaniline (15b) was prepared by Schmidt reaction of 2-chloro-3,5-dinitrobenzoic acid, prepared by nitration of 2-chlorobenzoic acid using 100% nitric acid in 96% sulfuric acid at temperatures up to 125 °C. 2-Chloro-3,5-dinitrobenzoic acid (12.3 g, 50 mmol) was suspended in 20% oleum (40 mL), cooled in an ice bath, and covered with dichloroethane (35 mL). Sodium azide (3.71 g, 57 mmol) was added in portions at such a rate that the temperature did not exceed 35–40 °C. The temperature was then raised slowly, and the reaction mixture was heated under reflux for 3 h. The solid dissolved with the evolution of nitrogen. The reaction mixture was cooled, and the dichloroethane was separated and discarded. The acid layer was poured into ice/water (400 mL). Filtration, washing with ice water, and drying at the pump overnight gave the required product **15b** as a yellow solid [10.0 g, 92%, mp 165 °C (lit.[19] 168 °C)], which was used without further purification.

2-Diazo-3-methyl-4,5,6-trinitrophenol (5a). 2-Amino-*N*,3,4,5,6-pentanitrotoluene (**17a**)[9] (0.95 g, 2.9 mmol) was suspended in dichloromethane (50 mL) and heated under reflux for 12 h with stirring. The reaction mixture was allowed to cool, and the yellow solid was filtered off. The filtrate was evaporated to dryness to give an orange solid. The combined solid products were recrystallized from dichloromethane (45 mL) to give a total of 0.50 g (68%) of yellow crystalline solid (mp 175 °C, explosion) identified as the diazophenol **5a** by its IR [2200, 1650 (diazophenol) 1570, 1540, 1390, 1365, 1340, 1320 cm^{-1} (NO_2)] and NMR [δ 2.84 (s, CH_3)].

Similar thermolysis of 3-amino-*N*,2,4,5,6-pentanitrotoluene **22**[9] by heating in dichloromethane under reflux gave a red oil (65%), which could not be further purified by crystallization or chromatography but whose IR and NMR spectra were consistent with a diazomethyltrinitrophenol.

4-Diazo-2-nitrophenol (7). Method A. 3,4-Dinitroaniline[1b] (2.0 g, 10.9 mmol) was added to glacial acetic acid (45 mL), and the reaction mixture was stirred at room temperature. Nitric acid (2.5 mL, 90%) and acetic acid anhydride (2.5 mL) were added sequentially, and the mixture was stirred at room temperature for 30 min. The resultant clear yellow solution was extracted with benzene (5 × 50 mL), and the extract was dried over anhydrous magnesium sulfate. Evaporation to dryness gave an orange liquid, which was further evacuated under high vacuum overnight. The resultant viscous liquid was triturated with a little acetone to give bronze colored crystals (0.70 g, 39%). Recrystallization from acetone gave bronze plates (mp 170 °C, explosion) identified as the diazophenol **7** by IR [2190, 1640 (diazophenol), 1620, 1340 cm^{-1} (NO_2)] and NMR [δ 8.88 (d, $J \approx 3$ Hz, H_3), 7.80 (dd, $J \approx 10$ Hz, $J \approx 3$ Hz, H_5), 6.45 (d, $J \approx 10$ Hz, H_6).

4-Diazo-2-nitrophenol (7). Method B. 3,4-Dinitroaniline[1b] (4.0 g, 21.8 mmol) was added to glacial acetic acid (90 mL), and the reaction mixture was stirred at room temperature. Nitric acid (5 mL, 90%) and acetic anhydride (5 mL) were added sequentially, and the mixture was stirred at room temperature for 30 min.[1b] The resultant clear yellow solution was poured into ice/water (400 mL) and extracted with benzene (6 × 75 mL). The extract was washed with distilled water (50 mL), dried over anhydrous magnesium sulfate, and evaporated to dryness at 25 °C to give *N*,3,4-trinitroaniline as a yellow solid, mp 94 °C (2.8 g, 56%), which was used immediately. The nitramine (0.68 g, 3.0 mmol) was added to dichloromethane (50 mL), and the mixture was heated under reflux overnight. Cooling and filtration gave the diazophenol **7** (0.40 g, 81%), which was recrystallized from acetone to give material identical in all respects with that prepared by other routes.[10]

2-Diazo-5-methyl-4,6-dinitrophenol (13a). 4-Amino-2,6-dinitrotoluene (**10a**) (0.60 g, 3.0 mmol) was dissolved in 96% sulfuric acid (36 mL) and glacial acetic acid (12 mL) and cooled in an ice bath. Nitric acid (1.8 mL, 90%) in glacial acetic acid (12 mL) was added dropwide and with stirring, and the solution was maintained at ice bath temperatures for 6 h before being placed in a refrigerator overnight. The solution was stirred at ice bath temperature for a further 4 h and was then extracted with dichloromethane (4 × 50 mL). The extract was washed with water (2 × 100 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a yellow oil (0.68 g, 78%) identified as 4-amino-*N*,2,3,6-tetranitrotoluene (**11**),[9] identified by its IR [3350 (NH), 1530, 1340, 1320 cm^{-1} (NO_2)] and NMR [δ 8.53 (s, 1, Ar H), 2.57 (s, 3, CH_3); nitramine proton obscured] and used immediately without purification. Dissolution in dichloromethane (50 mL), heating under reflux for 24 h, and evaporation to dryness gave the diazophenol **13a** (0.55 g, 81%), recrystallized from dichloromethane as red crystals (mp 178–179 °C, explosion) identified by its IR [2180, 1630 (diazophenol), 1610, 1570, 1540, 1525, 1340, 1310 cm^{-1} (NO_2)] and NMR [δ 9.00 (s, 1, Ar H), 2.43 (s, 3, CH_3)].

Prepared in the same manner from **10b**, **15a**, and **15b** were 2-diazo-5-chloro-4,6-dinitrophenol (**13b**) [51%, yellow solid, mp 178 °C dec, recrystallized from dichloromethane; IR 2220, 1628 (diazophenol), 1605, 1560, 1530, 1335, 1310 cm^{-1} (NO_2); NMR δ 9.18 (s, Ar H)], 2-diazo-3-methyl-4,6-dinitrophenol (**4a**) [75%, yellow solid, mp 139–141 °C dec, recrystallized from dichloromethane; IR 2195, 1630 (diazophenol), 1630, 1555, 1510, 1335, 1310 cm^{-1} (NO_2); NMR δ 8.87 (s, 1, Ar H), 2.91 (s, 3, CH_3)], and 2-diazo-3-chloro-4,6-dinitrophenol (**4b**) [65%, yellow solid, mp 154 °C dec, recrystallized from dichloromethane; IR 2200, 1650 (diazophenol), 1560, 1530, 1320 cm^{-1} (NO_2); NMR δ 8.95 (s, Ar H)]. The latter compound was also obtained in 57% yield when the nitration was carried out in 80% sulfuric acid at 0 °C. Nitration of 3-amino-2,5-dinitrotoluene (**21**) in acetic acid and sulfuric acid gave a red orange oil (50%). Attempts at purification by crystallization or chromatography proved unsuccessful, but the IR [2180, 2160, 1650, 1600, 1550, 1330 cm^{-1}] and NMR [δ 8.20 (s, 1 H, Ar H), 2.60 (s, 3 H, CH_3)] are consistent with a diazomethyldinitrophenol.

Thermolysis of 4-Amino-*N*,2,3,5,6-pentanitrotoluene (14a). The nitramine **14a** (0.50 g, 15 mmol) was dissolved in dichloromethane (50 mL) and heated under reflux. After 4 days essentially no reaction was discernible by NMR spectroscopy. Repetition of the thermolysis in chloroform (50 mL) for 60 h gave predominantly 4-amino-2,3,5,6-tetranitrotoluene (**12a**) (0.31 g, 72%); evaporation to dryness and recrystallization from chloroform gave **12a** as orange crystals (0.16 g, 37%). Thermolysis in chloroform containing 90% nitric acid or in carbon tetrachloride gave essentially the same result. When the nitramine **14a** (0.50 g, 1.5 mmol) was heated for 60 h in ethyl acetate or acetone (50 mL) under reflux and the reaction solution was evaporated to dryness, a yellow oily product (0.40 g) was obtained. Column chromatography (chloroform/silica) and recrystallization from chloroform gave **12a** (0.04 g) and 2,3,5,6-tetranitrotoluene (**19a**) (0.14 g, 34%) as a pale yellow solid (mp 150–152 °C) identified by IR [3045 (Ar CH), 1550, 1335 cm^{-1} (NO_2)] and NMR [δ 9.16 (s, 1 Ar H), 2.46 (s, 3, CH_3)].

Similar thermolysis of 4-chloro-*N*,2,3,5,6-pentanitroaniline (**14b**) gave unchanged nitramine or 4-chloro-2,3,5,6-tetranitroaniline (**12b**).

2-Chloro-*N*,3,4,5,6-pentanitroaniline (17b). 2-Chloro-3,5-dinitroaniline (**15b**) (2.0 g, 9.2 mmol) was dissolved in 96% sulfuric acid (60 mL) and cooled in an ice bath. Nitric acid (7.0 mL, 100%) was added dropwise with stirring, and the solution was allowed

(18) Wulfman, D. S.; Cooper, C. F. *Synthesis* **1978**, *12*, 924.
(19) Blanksma, J. J.; Verberg, G. *Recl. Trav. Chim. Pays-Bas* **1934**, *53*, 988.

to warm to room temperature. A yellow solid and an orange solid separated from the solution on standing overnight. Extraction with dichloromethane (5 × 100 mL), drying over magnesium sulfate, and evaporation of the solvent gave a red oil (2.20 g). Trituration with dichloromethane gave the nitramine **17b** as a yellow powder (1.33 g, 40%) identified by IR [3140 (NH), 1600, 1560, 1300, 1260 cm^{-1} (NO_2)] and NMR [δ 2.6 (NH)] and used without further purification. Evaporation of the dichloromethane and trituration of the residue with diethyl ether gave the diazophenol **4b** (0.43 g, 19%) also identified by IR and NMR.

2-Chloro-3,4,5,6-tetranitroaniline (18b). 2-Chloro-*N*,3,4,5,6-pentanitroaniline (**17b**) (1.10 g, 3.1 mmol) was suspended in 96% sulfuric acid (50 mL) at room temperature. Anisole (1.5 mL) was added, and the suspension was stirred overnight. Unlike other nitramine cleavage reactions, which turn very dark, the reaction mixture consisted of a yellow solid suspended in a green liquid phase. Extraction with dichloromethane (5 × 50 mL) followed by drying over magnesium sulfate, and evaporation of the solvent gave a yellow solid (0.93 g, 97%). Recrystallization from dichloromethane gave the amine **18b** as yellow needles, mp 163 °C, identified by IR [3460, 3360 (NH_2), 1620, 1570, 1530, 1350, 1330, 1280 cm^{-1} (NO_2)] and NMR [δ 8.4 (br s, NH_2)].

2-Diazo-5-methyl-3,4,6-trinitrophenol (20a). 4-Amino-2,3,5,6-tetranitrotoluene (**12a**) (1.0 g, 3.5 mmol) was dissolved in glacial acetic acid (30 mL); 90% nitric acid (2 mL) and acetic anhydride (2 mL) were added sequentially with stirring. Stirring was continued at room temperature for 1 h, and the reaction mixture was dissolved in benzene (200 mL) and washed with distilled water (3 × 100 mL). Drying over anhydrous sodium sulfate and evaporation to dryness gave a yellow solid, which was triturated with a little ether to give yellow crystals (0.35 g, 38%). Recrystallization from dichloromethane gave the diazophenol **20a** (mp 171 °C dec) identified by IR [2180, 1640 (diazophenol), 1600, 1560, 1535, 1360, 1340, 1320 cm^{-1} (NO_2)] and NMR [δ 2.27 (s, CH_3)].

Prepared in the same manner from **12b**, **18a**, and **18b** were 2-diazo-5-chloro-3,4,6-trinitrophenol (**20b**) [21%, yellow solid, mp 183–185 °C dec, from dichloromethane; IR 2180, 1640 (diazophenol), 1595, 1560, 1540, 1500, 1360, 1330, 1300 cm^{-1} (NO_2); no proton in the NMR], 2-diazo-3-methyl-4,5,6-trinitrophenol (**5a**), and 2-diazo-3-chloro-4,5,6-trinitrophenol (**5b**) [32%, yellow solid, mp 184 °C dec, recrystallized from dichloromethane; IR 2220, 1640 (diazophenol), 1590, 1570, 1550, 1480, 1390, 1355, 1335, 1310 cm^{-1} (NO_2); no proton in the NMR]. (The latter compound was also prepared by thermolysis of the nitramine **17b** in dichloromethane.) The ^{15}N-labeled **40–42** were prepared by exactly analogous methods.

3-Chloro-1,2,4,5-tetranitrobenzene (19b). 4-Chloro-*N*,2,3,5,6-pentanitroaniline (**14b**) (1.0 g, 2.8 mmol) was added to glacial acetic acid (30 mL), 90% nitric acid (2 mL) and acetic anhydride (2 mL) were added sequentially and with stirring at room temperature. After 1 h the solution was dissolved in benzene (200 mL) and washed with water (3 × 100 mL). Drying over magnesium sulfate and evaporation of the solvent gave an orange oil. Trituration with dichloromethane and ether gave a yellow solid (0.20 g, 25%), recrystallized from those solvents to give 3-chloro-1,2,4,5-tetranitrobenzene (**19b**), mp 144–146 °C, identified by IR [1550, 1355 cm^{-1} (nitro)] and NMR [δ 9.4 (s, Ar H)].

Nitration of 2-Chloro-3,5-dinitroaniline (15b) in Oleum. 2-Chloro-3,5-dinitroaniline (**15b**) (1.0 g, 4.6 mmol) was dissolved in 20% oleum (30 mL) and cooled in an ice bath. Nitric acid (3.5 mL, 100%) was added dropwise with stirring over about 10 min. The solution was allowed to warm to room temperature and was stirred overnight. Extraction with dichloromethane (5 × 50 mL) gave only a small amount (0.05 g) of red tar. The reaction mixture was quenched on ice (200 mL) and extracted with dichloromethane (5 × 50 mL). Drying over anhydrous sodium sulfate and evaporation of the solvent gave an orange oil (0.70 g), which on trituration with dichloromethane yielded an orange/yellow solid (0.35 g, 36%) identified by IR and NMR as 2-diazo-4,6dinitrophenol (**3**).

Nitration of 4-chloro-3,5-dinitroaniline (**10b**) in oleum under the same conditions gave 2-diazo-5-chloro-4,6-dinitrophenol (**13b**), while 3,5-dinitroaniline (**1**) gave only a tarry residue from which no identifiable product was isolated.

2,3,4,6-Tetranitroaniline (27). 2,3-Dinitroaniline (**26**)[1b] (0.50 g, 2.7 mmol) was dissolved in 96% sulfuric acid (30 mL) and cooled in an ice bath. Nitric acid (3 mL, 70%) was added dropwise with stirring, and stirring was continued at 0–5 °C for 24 h. The reaction solution was extracted with dichloromethane (5 × 50 mL), the extract dried over magnesium sulfate and evaporated to dryness to give a yellow solid (0.53 g, 73%). Washing with dichloromethane and recrystallization from that solvent gave the amine **27** as yellow crystals, mp 221 °C (lit.[20] mp 220 °C), identified by IR [3450, 3340 (NH_2), 1640, 1575, 1530, 1340, 1320, 1290 cm^{-1} (NO_2)] and NMR [δ 9.28 (s, 1 H, ArH), 8.8 (br s, 2 H, NH_2)].

2-Diazo-4-methyl-3,5-dinitrophenol (36). 3-Amino-2,6-dinitrotoluene (**32**)[5] (0.50 g, 2.5 mmol) was dissolved in 96% sulfuric acid (25 mL) at room temperature, and 90% nitric acid (1 mL) was added dropwise with stirring. Stirring was continued for 24 h, and the reaction solution was extracted with dichloromethane (5 × 50 mL). The extract was dried over magnesium sulfate and evaporated to dryness to give a red oil (0.40 g), which partially solidified on standing. The presence of a diazophenol was confirmed by IR; NMR indicated the presence of two compounds in the ratio 4:1. Trituration with a little ethanol gave the major product as an orange crystalline solid (0.09 g, mp 157 °C dec) identified as the diazophenol **36** by IR [2130, 1620 (diazophenol), 1585, 1530, 1520, 1320 cm^{-1} (NO_2)] and NMR [δ 7.70 (s, 1 H, Ar H), 2.30 (s, 3 H, CH_3)]. The minor product could not be isolated. Nitration of 3-amino-4,6-dinitrotoluene (**33**)[5] and 3-amino-2,4-dinitrotoluene (**34**)[5] under the same conditions gave similar mixtures of products.

Acknowledgment. Part of this work was performed during an exchange of scientific staff under the Technical Cooperation Program (TTCP). We are pleased to acknowledge the helpful discussion and suggestions of our colleagues including Dr. A. T. Nielsen (NWC) and Drs. R. W. Read and R. J. Spear (MRL). Mass spectra of ^{15}N-labeled materials were recorded by Dr. A. G. Moritz (MRL).

Registry No. **3**, 4682-03-5; **4a**, 70343-16-7; **4b**, 97564-29-9; **5a**, 97564-27-7; **5b**, 97564-31-3; **7**, 18396-83-3; **10a**, 19406-51-0; **10b**, 84388-94-3; **11**, 84432-52-0; **12a**, 84432-53-1; **12b**, 102367-92-0; **13a**, 82177-77-3; **13b**, 97564-30-2; **14a**, 84432-54-2; **14b**, 102434-50-4; **15a**, 35572-78-2; **15b**, 88140-44-7; **17a**, 91125-10-9; **17b**, 102434-49-1; **18a**, 84432-57-5; **18b**, 102367-93-1; **19a**, 102367-91-9; **19b**, 102367-94-2; **20a**, 97564-28-8; **20b**, 97564-32-4; **21**, 65321-68-8; **22**, 84432-55-3; **26**, 602-03-9; **27**, 3698-54-2; **32**, 10202-92-3; **33**, 5267-27-6; **34**, 70343-06-5; **36**, 102367-95-3; TNT, 118-96-7; 2-chloro-3,5-dinitrobenzoic acid, 2497-91-8; diazomethyltrinitrophenol, 102367-97-5; 3,4-dinitroaniline, 610-41-3; diazomethyldinitrophenol, 102367-99-7.

(20) Forster, A.; Coulson, W. *J. Chem. Soc.* **1922**, 1992.