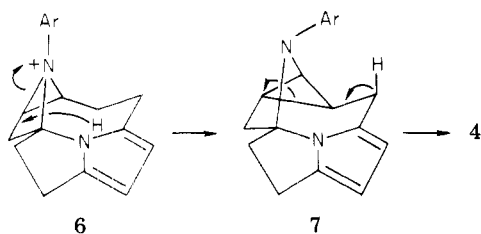


tractive structural candidate. In fact, an X-ray crystallographic structure determination (see supplementary material Table II and Figure 1) confirmed this deduction and established structure 4 as the correct one for this compound (cf. Table II). The number of modes of formation of this isomer from compound 3 is limited by Bredt's rule. Thus, the simple process of two successive 1,3-hydrogen shifts in compound 3 which leads directly to structure 4 must be eliminated. On the other hand, protonation of the double bond aided by participation of the phenyl-substituted nitrogen gives rise to the aziridinium ion 6. This might well be the intermediate leading to compound 4.

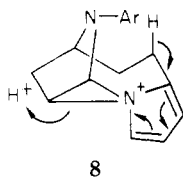


### Experimental Section

13-(*p*-Bromophenyl)-13,14-diazatetracyclo-[8.2.1.1<sup>4,7</sup>.0<sup>1,14</sup>]tetradeca-2,4,6-triene (4). Compound 1<sup>1</sup> (200 mg, 0.86 mmol) was dissolved in 20 mL of glacial HOAc and heated at 100 °C under a nitrogen atmosphere for 1.5 h. The mixture was cooled and poured into a cold, concentrated NH<sub>4</sub>OH solution. The product was extracted with CHCl<sub>3</sub> (3 × 25 mL), and the extracts were dried over anhydrous K<sub>2</sub>CO<sub>3</sub>. Chromatography of the crude product on Brockmann grade II silica gel, using 1:1

(3) Systematic absences allowed the space group to be either *P*<sub>2</sub><sub>1</sub>/*m* or *P*<sub>2</sub><sub>1</sub>. Solution and refinement of the structure showed that the latter is the correct choice.

(4) A referee suggested the possible intermediacy of structure 8 followed by the rearrangements shown. An examination of molecular models indicates this to be a rather highly strained structure, in comparison to our proposed structure 7 which requires no significant introduction of strain.



benzene-cyclohexane as eluent, gave 30 mg of a yellow oil which gradually solidified. Further elution with CH<sub>2</sub>Cl<sub>2</sub> gave a trace of *p*-bromoaniline identified by its *R*<sub>f</sub> value from thin-layer chromatography and its mass spectrum. The product was further purified by sublimation (120 °C (0.1 mm)) to give a yellow solid: 160 mg (80%); mp 142–143.5 °C; mass spectrometric mol wt 340 and 342; <sup>1</sup>H NMR δ 1.8–3.2 (m, 8 H), 4.70 (br t, 1 H), 5.47 (dd, 1 H), 5.79 (d, 1 H), 6.0–6.4 (m, 4 H), 7.11 (d, 2 H); UV (isooctane), λ<sub>max</sub> (log ε) 253 (3.86), 292 (3.85), 301 (sh) (3.78). Anal. Calcd for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>Br: C, 63.36; H, 5.03; N, 8.21. Found: C, 63.25; H, 5.03; N, 8.14.

**X-ray Data Collection, Structure Solution, and Refinement.** A single crystal of 4 was sealed in a thin-walled glass capillary and placed on an Enraf-Nonius CAD-4 diffractometer. Final lattice parameters as determined from a least-squares refinement of the angular settings of 12 accurately centered reflections (2θ > 30°) are given in Table I.

Data were taken on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the θ-2θ scan technique. The scan rate was variable and was determined by a fast (20° min<sup>-1</sup>) prescan. One independent quadrant of data was collected to 2θ ≤ 40°. This produced 888 independent observed reflections (*I* > 3σ(*I*)). A complete account of the data collection procedure and diffractometer parameters has been given previously.<sup>2</sup>

The existence of two molecules per unit cell in the space group *P*<sub>2</sub><sub>1</sub> imposed no crystallographic symmetry.<sup>3</sup> The position of the bromine atom was deduced from a Patterson map, and a subsequent difference Fourier map calculation revealed the positions of all remaining nonhydrogen atoms. In the final cycles of refinement the bromine atom was treated with anisotropic thermal parameters, while the nitrogen and carbon atoms were dealt with isotropically. Hydrogen atoms were placed in calculated positions and unobserved reflections were not used. The final *R* values were

$$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.060$$

$$R_2 = \{ \sum(|F_o| - |F_c|)^2 / \sum F_o^2 \}^{1/2} = 0.062$$

The largest parameter shifts in the final cycle were less than 0.10 of their esd's, and a difference Fourier map showed no unaccounted electron density. The final values of the positional and thermal parameters are given in supplementary material Table II.

**Registry No.** 1, 59547-40-9; 4, 70288-27-6.

**Supplementary Material Available:** Figure 1 with numbering and Tables II and III containing atomic coordinates and bond lengths and angles (3 pages). Ordering information is given on any current masthead page.

## Synthetic Routes to Aminodinitrotoluenes

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Synthetic routes to the aminodinitrotoluenes have been investigated and several useful new methods developed. A procedure for selective hydrolysis of polynitro *N*-acyltoluidines permits facile separation of the nitration isomer mixtures. Products formed by reaction of ammonia with isomeric trinitrotoluenes, as well as those from reduction of 2,4,6-trinitrotoluene with hydrogen sulfide, have been separated and identified.

Aminodinitrotoluenes have been identified in our work as major components of waste waters resulting from the manufacture of 2,4,6-trinitrotoluene ( $\alpha$ -TNT). They are also formed by ammonolysis and reduction of TNT iso-

mers. In order that their toxicological and explosive properties could be evaluated, convenient synthetic routes to these substances were required. This report describes some new syntheses of aminodinitrotoluenes and im-

Table I. Aminodinitrotoluenes

compd	isomer <sup>a</sup> NH <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub>	mp <sup>b</sup> (dec <sup>c,f</sup> ), °C	synthetic method <sup>d</sup>	ref <sup>e</sup>
1	2,3,4	131-131.5	C <sup>f</sup>	f, 1-3
2	2,3,5	217-218 (320)	A, C <sup>f</sup>	f, 1, 4-8
3	2,3,6	151 (300)	A, f C	f, 1, 7, 9, 29
4	2,4,5	191-191.5	C <sup>f</sup>	f, 2, 3
5	2,4,6	175-176 <sup>f</sup> (307)	B, E <sup>f</sup>	f, 5, 10-12, 14, 15
6	6,2,3	222 <sup>f</sup>	C <sup>f</sup>	f, 13, 29
7	3,2,4	94 (280)	A <sup>f</sup>	f, 16-21
8	3,2,5	127-128 <sup>f</sup> (350)	E <sup>f</sup>	f
9	3,2,6	134	A, f C, D <sup>f</sup>	f, 9, 22
10	3,4,5	141	C	23
11	5,2,3	165	C	23
12	5,2,4	197-199 <sup>f</sup> (320)	A, f D <sup>f</sup>	f, 8, 16-18, 21, 24
13	4,2,3	125.5-126	C	25, 27, 28
14	4,2,5	190-191	C	25, 27
15	4,2,6	171-172 <sup>f</sup> (325)	B, f E	f, 10-14, 29-37
16	4,3,5	176-177 <sup>f</sup> (250) <sup>g</sup>	A, f C	f, 1, 8, 23, 25, 26

<sup>a</sup> Numbers represent toluene substituents with position of amino group listed first, followed by positions of the two nitro groups (IUC numbering). <sup>b</sup> Highest reported melting point, including values of the present work.

<sup>c</sup> Decomposition temperatures are exothermic maxima or initial decomposition temperatures obtained by differential thermal analysis. <sup>d</sup> Synthetic methods: (A) reaction of ammonia with the appropriate trinitrotoluene or halo-, hydroxy-, or alkoxy-substituted dinitrotoluene; (B) reduction of 2,4,6-trinitrotoluene; (C) nitration and subsequent hydrolysis of the corresponding *N*-acetyl or *N*-toluenesulfonylnitrotoluidine; (D) reaction of a dinitrotoluene with hydroxylamine; (E) reaction of the dinitrotoluic acid with hydrazoic acid (Schmidt reaction).

<sup>e</sup> Major representative references; not a complete listing.

<sup>f</sup> Present work. <sup>g</sup> Initiation of exotherm occurs at this temperature; no sudden exotherm or gas evolution was noted.

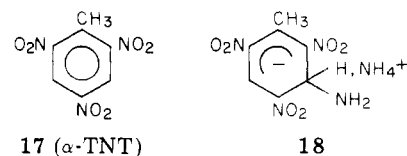
improvements in existing methods, in addition to some new chemistry of their precursors and related nitro aromatics.

Of the 16 possible isomeric aminodinitrotoluenes, 15 have previously been reported. A synthesis of the remaining unknown one (3-amino-2,5-nitrotoluene) is described herein. A listing of the isomers with methods of synthesis is found in Table I.<sup>1-37</sup>

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Five principal synthetic routes to aminodinitrotoluene are useful: (1) reaction of ammonia with isomeric trinitrotoluenes and halo-, hydroxy-, or alkoxy-substituted dinitrotoluenes, (2) reduction of 2,4,6-trinitrotoluene, (3) nitration and subsequent hydrolysis of *N*-acetyl or *N*-toluenesulfonylnitrotoluidines, (4) reaction of dinitrotoluenes with hydroxylamine, and (5) reaction of dinitrotoluic acids with hydrazoic acid (Schmidt reaction). The following discussion describes our results in this order.

**Reaction of trinitrotoluenes with ammonia** leads to aminodinitrotoluenes, often in high yield.<sup>4,9,16-20,29</sup> The products do not react further with ammonia to yield diamino compounds. 2,4,6-Trinitrotoluene ( $\alpha$ -TNT, 17) in



which all nitro groups are meta oriented is exceptional, however, in that several workers report the isolation of an unstable, red, crystalline addition compound in which are contained two ammonia molecules (unidentified; possibly 18) and from which no aminodinitrotoluene could be obtained.<sup>38-45</sup> The other five TNT isomers produce

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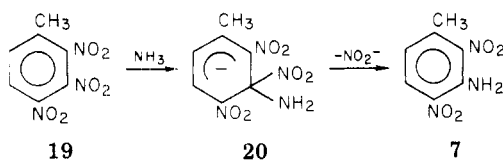
Table II. Proton Nuclear Magnetic Resonance Parameters for Selected Aminodinitrotoluenes and Related Compounds

compd	toluene substitution	chemical shifts, $\delta^{a,b}$								$J$ values, Hz	
		H-2	H-3	H-4	H-5	H-6	CH <sub>3</sub>	NH <sub>2</sub> <sup>c</sup>	NH		OH
17	2,4,6-trinitro-		9.01		9.01		2.69				$J_{3\text{Me}} = 0.43$
2	2-amino-3,5-dinitro-			8.86		8.09	2.45	7.72			$J_{46} = 2.84$ $J_{4\text{Me}} = 0.56$ $J_{6\text{Me}} = 0.88$ $J_{45} = 9.11$
3	2-amino-3,6-dinitro-			8.17	7.02		2.31	7.29			$J_{36} = 8.82$ $J_{5\text{Me}} = 0.24$ $J_{6\text{Me}} = 0.55$ $J_{46} = 2.48$ $J_{4\text{Me}} = 0.58$ $J_{6\text{Me}} = 0.73$ $J_{36} = 0.30$ $J_{3\text{Me}} = 0.22$ $J_{6\text{Me}} = 0.84$ $J_{2\text{Me}} = 0.80$
5	2-amino-4,6-dinitro-		7.82		7.82		2.31	5.91			
7	3-amino-2,4-dinitro-			7.73		7.37	2.46	6.22			
8	3-amino-2,5-dinitro-										
12	5-amino-2,4-dinitro-		8.89			7.03	2.58	7.69			
16	4-amino-3,5-dinitro-	8.42				8.42	2.41	8.35			
15	4-amino-2,6-dinitro-		7.40		7.40		2.30	5.72			
24	4-(hydroxylamino)-2,6-dinitro-		7.66		7.66		2.39		8.60	8.35	$J_{\text{NH-OH}} = 2.0$ $J_{3\text{Me}} = 0.3$
25	2-(hydroxylamino)-4,6-dinitro-		8.09		8.25		2.35		8.46	8.42	$J_{\text{NH-OH}} = 2.0$ $J_{23} = 2.3$

<sup>a</sup> The expected multiplicities and integrated intensities are observed for all signals. <sup>b</sup> 100.1 MHz, acetone-*d*<sub>6</sub> solvent, tetramethylsilane reference. <sup>c</sup> The NH<sub>2</sub> signals appear as broad singlets (~15 Hz FWHM).

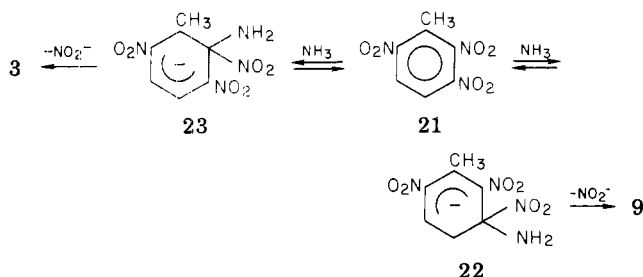
aminodinitrotoluenes by displacing a nitro group which is ortho or para to another nitro group or groups.

2,3,4-Trinitrotoluene ( $\beta$ -TNT, **19**) reacts with ammonia



in ethanol at reflux to yield 3-amino-2,4-dinitrotoluene (**7**) in 90–95% yield.<sup>16–20</sup> The reaction proceeds through a Meisenheimer adduct (**20**) which slowly loses nitrite ion to yield product.<sup>42,45</sup> In the present study analysis of the crude product by gas chromatography mass spectroscopy (GC/MS) indicates a single component; reactant TNT and isomeric aminodinitrotoluenes are absent. Similarly, it is observed that reaction of ammonia in ethanol at 25 °C with 2,3,5-, 2,4,5-, and 3,4,5-trinitrotoluenes yields principally 2-amino-3,5-dinitrotoluene (**2**), 5-amino-2,4-dinitrotoluene (**12**), and 4-amino-3,5-dinitrotoluene (**16**), respectively.<sup>4,16–18</sup>

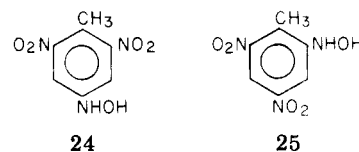
Exceptional behavior is observed in the reaction of 2,3,6-trinitrotoluene (**21**) with refluxing ethanolic ammonia.



The crude reaction product, rather than being homogeneous, is found to contain, among other products, 2-amino-3,6-dinitrotoluene (**3**) and 3-amino-2,6-dinitrotoluene (**9**) in a 1:1 ratio as well as trace amounts of 6-amino-2,3-dinitrotoluene (**6**) by GC/MS analysis. (Some ethoxydinitrotoluenes are formed as well.) Pure **3** is obtained by recrystallization of the crude product from

ethanol; attempts to obtain pure **9** from the filtrate by fractional crystallization, however, yields a constant-melting product containing a mixture of products, including **3** and **9**. (We have developed an alternative superior synthesis of **9**, described below.) Another exceptional feature of the reaction of TNT isomer **21** with ammonia is that it is the only example in this series in which displacement of a nitro group meta to another nitro group is observed. The result may be explained by a steric crowding destabilization of expected Meisenheimer precursor **22**, relative to isomer **23**. This factor, caused by crowding of groups ortho to the 2-nitronate anion in **22**, is absent in **23** and in anions derived from the other TNT isomers.<sup>42,45</sup>

**Reduction of 2,4,6-trinitrotoluene (17,  $\alpha$ -TNT)** has been studied extensively by employing a variety of reducing agents.<sup>5,10–13,30–37,46</sup> In most cases 4-amino-2,6-dinitrotoluene (**15**) is the principal product. We examined the reduction with hydrogen sulfide in the presence of a catalytic amount of ammonia and found the product distribution to be solvent dependent. In dioxane solvent<sup>10</sup> reduction of one nitro to amino occurs and 4-amino-2,6-dinitrotoluene (**15**) and 2-amino-4,6-dinitrotoluene (**5**) are the isolated products formed in a 99:1 ratio (<sup>1</sup>H NMR assay). In ethanol solvent attack at the 4 position is favored, but reduction is less complete. Products, in addition to unreacted TNT (22%), were 4-(hydroxylamino)-2,6-dinitrotoluene (**24**, 44%), **15** (22%), **5** (4%), and 4,6-di-



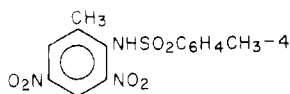
nitro-2-(hydroxylamino)toluene (**25**, 8%), the last not previously identified as a reduction product of  $\alpha$ -TNT. Structure assignments and assay of the components of the mixture were established by column chromatography, NMR spectra (Table II), and mass spectroscopy. A product, mp 155 °C, obtained by hydrogen sulfide reduction of  $\alpha$ -TNT in ethanol and described as pure 2-

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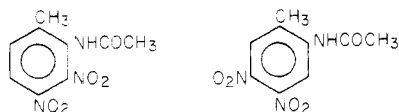
amino-4,6-dinitrotoluene 5,<sup>5,12</sup> has been shown by us to be a mixture containing principally 5 and the 4-hydroxylamino compound 24. Pure 5 is difficult to prepare by reduction of TNT; it is more conveniently obtained by the Schmidt reaction method.<sup>14</sup> The reactions of 2,3,4-trinitrotoluene and 2,4,5-trinitrotoluene with ammonium sulfide to yield aminodinitrotoluenes 7 and 12, respectively, probably involve principally nitrite ion displacement by ammonia rather than a reduction as reported.<sup>16,33</sup>

**Nitration and subsequent hydrolysis of *N*-acetyl- or *N*-toluenesulfonylnitrotoluidines** is the method employed for preparation of most aminodinitrotoluenes (Table I, method C). We have developed some convenient, improved procedures for these preparations. 2-Amino-3,5-dinitrotoluene (2) is available by ammonolysis of 2,3,5-trinitrotoluene ( $\epsilon$ -TNT), but owing to the difficulty of synthesizing the latter compound by routes other than oxidation of 2, this procedure is of little value. However, 2 may be conveniently prepared in three steps from 2-[*N*-(4-toluenesulfonyl)]toluidine. Nitration proceeds in two steps (92% overall yield) to the 3,5-dinitro derivative 26, which is then hydrolyzed to 2.<sup>6</sup>



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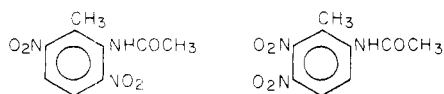
Nitration of an *N*-substituted toluidine to form a single dinitro derivative such as 26 in very high overall yield is not always observed. One may encounter difficult isomer separations when *N*-(4-toluenesulfonyl)- or *N*-acetamidodinitrotoluenes are nitrated. For example, nitration of 2-acetamido-4-nitrotoluene provides a mixture of 3,4- and 4,5-dinitro-2-acetamidotoluenes (27 and 28 in a 2:3 ratio). A partial separation of these isomers can be



27

28

achieved by fractional crystallization (with large losses of material). However, a facile and nearly quantitative separation is possible by fractional solvolysis of these intermediates. Under appropriate reaction conditions an acetamido group ortho to a nitro group has been found to hydrolyze much more slowly than one in a more remote position. Thus, the mixture of 27 and 28 dissolved in 50% aqueous sulfuric acid at 25 °C yields principally the hydrolysis product of 28, 2-amino-4,5-dinitrotoluene (4); the product mixture is easily separated owing to the large solubility differences between 4 and 27 in selected solvents. The unhydrolyzed 27 when subjected to more vigorous hydrolysis conditions (50% sulfuric acid at 80 °C) yields 2-amino-3,4-dinitrotoluene (1). Similarly, a mixture of nearly equal amounts of isomers 29 and 30 easily afforded pure 2-amino-3,6-dinitrotoluene (3) and 6-amino-2,3-dinitrotoluene (6) by the fractional solvolysis procedure.

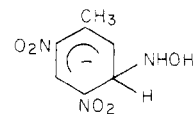


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**Reaction of *m*-dinitroarenes with hydroxylamine** in basic medium is an infrequently employed method for synthesis of aromatic amines developed years ago by Meisenheimer and Patzig.<sup>46</sup> These authors prepared 3-

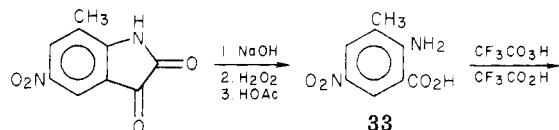
amino-2,6-dinitrotoluene (9) from 2,6-dinitrotoluene by this method in 10–15% yield. An improvement of this procedure was developed by Katritzky and co-workers to provide 9 in 46% yield.<sup>47</sup> However, these procedures are not applicable to the preparation of isomeric 5-amino-2,4-dinitrotoluene (12) from 2,4-dinitrotoluene; dark, unstable products result. We have prepared both aminodinitrotoluenes 9 and 12 by an alternate procedure—reaction of the appropriate TNT isomers with ammonia—but these precursors are not readily available in large quantities. A more convenient synthesis of 12 is a new modification of Meisenheimer's method which was developed in the present work; it employs a low reaction temperature and the very convenient reactant 2,4-dinitrotoluene to permit large-scale preparation of pure 12 in one step (22% yield). These reactions are believed to proceed through a Meisenheimer adduct (e.g., 31) which undergoes reduction to the amine.<sup>48</sup>



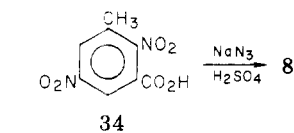
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**The Schmidt synthesis of aminodinitrotoluenes from dinitrotoluic acids** was introduced by Orlova and co-workers, who prepared isomers 5 and 15 by this convenient one-step method in high yield (90–98%);<sup>14</sup> we have confirmed these results. This method is much superior to the Hofmann reaction which, when applied to the same reactant acids, gives poor overall yields of aminodinitrotoluenes (10–30% in three steps).<sup>15</sup>

The only previously unreported aminodinitrotoluene, 3-amino-2,5-dinitrotoluene (8), has now been prepared in six steps from *o*-toluidine. 7-Methyl-5-nitrosatin (32)<sup>49</sup> was saponified and oxidized to form 2-amino-3-methyl-5-nitrobenzoic acid (33, 96%). Emmons oxidation<sup>50</sup> of 33 to 34 was followed by the Schmidt conversion to 8 (95%).



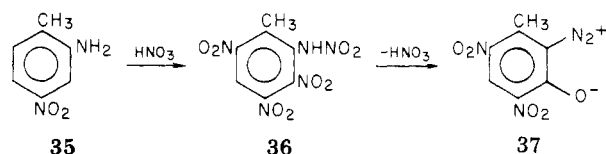
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The reaction of 2-methyl-5-nitroaniline (35) with fuming



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nitric acid (90%) has been reported by Kapil to produce 2-amino-4,6-dinitrotoluene (5); mp 160 °C.<sup>51</sup> (We have found authentic 5 to melt at 175–176 °C.) In our hands, Kapil's procedure gave a very sensitive explosive com-

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(48) (a) Gitis, S. S.; Pankova, N. A.; Kaminskii, A. Ya.; Kaminskaya, E. G. *Zh. Org. Khim.* 1969, 5, 65. (b) Lakomova, N. A.; Grudtsyn, Yu. D.; Gitis, S. S. *Ibid.* 1974, 10, 1046.

(49) Cassebaum, H. *J. Prakt. Chem.* 1964, 23, 301.

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pound; mp 152–154 °C (with rapid decomposition followed by an explosion with a flash; impact sensitivity less than 10 cm with a 2.5-kg weight). On the basis of NMR, mass spectra, and infrared spectra, the material is tentatively identified as 2-diazo-4,6-dinitro-3-methylphenol (37). Glowiak prepared an isomer, 4-diazo-2,6-dinitro-3-methylphenol, having similar properties.<sup>52,53</sup> The study of Scilly and co-workers suggests that the reaction may involve a nitramine intermediate (36).<sup>54</sup>

The aminodinitrotoluenes are rather stable substances. The decomposition temperature (first exotherm) was established by differential thermal analysis for each of the isomers 2, 3, 5, 7, 8, 12, 15, and 16 (values listed in Table I). Measured impact sensitivities of these compounds were greater than 180 cm, the limit of the instrument, compared to a value of 75 cm for  $\alpha$ -TNT; an exception is 4-amino-2,6-dinitrotoluene (15), 169 cm.

High-resolution <sup>1</sup>H NMR spectra of eight aminodinitrotoluenes have been determined (2, 3, 5, 8, 12, 15, 16). Their chemical shifts and coupling constants and those of 2,4,6-trinitrotoluene (17), 4-(hydroxylamino)-2,6-dinitrotoluene (24), and 2-(hydroxylamino)-4,6-dinitrotoluene (25) are given in Table II. The spectra are in agreement with structure assignments. The weak couplings between each ring hydrogen and the methyl group ( $J < 1$  Hz) have been assigned.

### Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 137 instrument; <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined on a Varian XL-100 spectrometer with a Transform Technology TT-100 pulsed Fourier transform system. Proton and <sup>13</sup>C chemical shift measurements were determined at ca. 30 °C and are referenced to a tetramethylsilane internal standard. Mass spectra were determined on a Hitachi Model RMU-6E. Melting points are corrected. Elemental analyses and molecular weights (vapor osmometry) were determined by Galbraith Laboratories.

Differential thermal analysis measurements were determined on a Perkin-Elmer Model DSC-1B instrument. Samples of 2–6 mg were used and temperature curves and gas evolution curves plotted. The heating rate was 10 °C/min. Decomposition temperatures are listed in Table I. Endotherms correspond closely to observed capillary melting points. Initial exothermic maxima (usually sharp, as with  $\alpha$ -TNT) are considered decomposition temperatures and are usually accompanied by gas evolution at the same temperature. Neither gas evolution nor a sudden exotherm was observed with 4-amino-3,5-dinitrotoluene and 2-amino-3,5-dinitrotoluene. An exotherm slowly increasing with temperature was noted with these compounds; decomposition temperatures listed in Table I for these materials are measured at the onset of the exotherm and are therefore lower than values reported for the other compounds. Impact sensitivities of all samples were determined as 50% positive values from 25 shots by using an impact tester (Bureau of Mines design) equipped with a 2.5-kg weight. Sample weight per shot was 35 ± 2 mg. Samples were placed on sandpaper, 5/0 grit carborundum.

Gas chromatographic analysis was performed with a Hewlett Packard Model 5711 instrument equipped with a flame ionization detector; columns were 6 ft × 2 mm i.d. packed with 10% Dow DC-200 on Chromosorb W-HP.

#### Reaction of TNT Isomers with Ethanolic Ammonia.

**5-Amino-2,4-dinitrotoluene (12)** was prepared by treating 2,4,5-trinitrotoluene ( $\gamma$ -TNT) with excess ethanolic ammonia at 25 °C according to the procedure of Hepp;<sup>17</sup> recrystallization from acetic acid gave a purified product (48% yield, mp 197–199 °C; lit.<sup>24</sup> mp 196.5–197.5 °C). Similarly, **4-amino-3,5-dinitrotoluene (16)** was prepared from 3,4,5-trinitrotoluene ( $\delta$ -TNT) and recrystallized from ethanol (61% yield, mp 176–177 °C; lit.<sup>26</sup> mp

172 °C). **3-Amino-2,4-dinitrotoluene (7)** was prepared from 2,3,4-trinitrotoluene (19,  $\beta$ -TNT) in refluxing ethanolic ammonia according to a modified Hepp procedure (mp 92–93 °C, 79% yield, after recrystallization from aqueous acetic acid (20% water); lit.<sup>17,19</sup> mp 94 °C). The unrecrystallized products were assayed by GC/MS and found to contain only one component (reactant TNT absent). **2-Amino-3,6-dinitrotoluene (3)** was prepared by heating 2,3,6-trinitrotoluene ( $\eta$ -TNT) with excess ethanolic ammonia and heating under reflux, a modification of the procedure of Körner and Contardi;<sup>9</sup> the product was purified by recrystallization from ethanol (mp 148–151 °C; lit.<sup>7,9,29</sup> mp 151 °C). The crude unrecrystallized product was found to be a mixture by GC/MS which contained much 3-amino-2,6-dinitrotoluene (9) (see discussion in text).

**Reduction of 2,4,6-Trinitrotoluene with Hydrogen Sulfide in Dioxane Solvent. 4-Amino-2,6-dinitrotoluene (15).** 2,4,6-Trinitrotoluene (100 g, 0.44 mol) in 250 mL of dioxane was treated with concentrated ammonium hydroxide (0.5 mL) and hydrogen sulfide bubbled through, keeping the temperature below 40 °C until no further exothermic reaction was observed. Sulfur was removed by filtration. The product was isolated as its hydrochloride salt by passing dry hydrogen chloride into the filtrate to yield 38 g (37%) of 15 hydrochloride; mp 169–171 °C (lit.<sup>10</sup> mp 172 °C). The salt was converted to the free base by treatment with aqueous sodium hydroxide. Recrystallization of the crude product from ethanol gave crystals (80% recovery); mp 167–168 °C (lit. mp 169 °C,<sup>15</sup> 171–172 °C<sup>46</sup>). Analysis of the crude product (obtained by evaporation of the filtrate to dryness before HCl treatment) by proton NMR indicated a mixture of 4-amino-2,6-dinitrotoluene (15) and 2-amino-4,6-dinitrotoluene (5) in a ratio of 99:1, in addition to a small amount of 4-(hydroxylamino)-2,6-dinitrotoluene (24).

**Reduction of 2,4,6-Trinitrotoluene with Hydrogen Sulfide in Ethanol Solvent.** 2,4,6-Trinitrotoluene (100 g, 0.44 mol) suspended in 500 mL of absolute ethanol containing 0.5 mL of concentrated ammonium hydroxide was treated with a rapid stream of hydrogen sulfide gas for 1 h, keeping the reaction temperature at 25–30 °C by ice-bath cooling. The reaction mixture was filtered to remove sulfur and the filtrate was diluted with water (1 L) to yield 64.8 g of product mixture; mp 100–120 °C. Assay of this mixture by column chromatography on silica (elution with benzene) revealed three principal bands (gravimetric analysis): (1) unreacted TNT (23%); (2) a mixture of 4-amino-2,6-dinitrotoluene (15) and 2-amino-4,6-dinitrotoluene (5) in a ratio of ca. 9:1 by NMR and gas-liquid chromatography assay (28% total); and (3) a mixture of 2-(hydroxylamino)-4,6-dinitrotoluene (25) and 4-(hydroxylamino)-2,6-dinitrotoluene (24) (49% total). The mixtures of 15 and 5 and of 24 and 25 could not be separated by thin-layer or column chromatography on silica or alumina. The assay was established more accurately by examining the <sup>1</sup>H NMR spectrum of the crude reaction mixture and gave the following values: TNT (22%), 15 (22%), 5 (4%), 24 (44%), 25 (8%); measurements were made in (CD<sub>3</sub>)<sub>2</sub>CO solvent by using both methyl and aryl signals for integration. Spectra of pure components are summarized in Table II.

**4-(Hydroxylamino)-2,6-dinitrotoluene (24).** A 60.0-g aliquot of the above product mixture from reduction of  $\alpha$ -TNT with hydrogen sulfide in ethanol was fractionally extracted with refluxing benzene in a Soxhlet extractor. After four single extractions of 500 mL each (which removed most of the 15 and 5), the remaining solid was extracted continuously until all was extracted (1.5 h). Cooling of the final extract deposited 11.7 g of crystalline product which assayed 90% 24 by thin-layer chromatography; recrystallization from benzene gave very pure 24: mp 143–147 °C (lit.<sup>32</sup> mp 143–145 °C); mol wt calculated for C<sub>7</sub>H<sub>7</sub>N<sub>3</sub>O<sub>5</sub> 213.15; found (mass spectrometry) 213 (parent peak).

**2-Amino-3,4-dinitrotoluene (1) and 2-Amino-4,5-dinitrotoluene (4).** To a mixed-acid solution (prepared from 418 mL of 96% sulfuric acid and 261 mL of 90% nitric acid) cooled to 5 °C was added (in small portions during 25 min) 97.1 g of 2-methyl-5-nitroacetanilide, maintaining the temperature at 4–7 °C. After addition, the temperature was allowed to rise to 15 °C, at which point the mixture was poured on 2.5 L of crushed ice. The light yellow precipitate was filtered, washed thoroughly with water, and dried under vacuum to yield 106.7 g (91%) of crude product containing about 40% 2-acetamido-3,4-dinitrotoluene (27)

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and 60% 2-acetamido-4,5-dinitrotoluene (**28**) (GC/MS assay). The crude product was stirred with 675 mL of 50% sulfuric acid for 25 min at 25 °C. The resulting mixture was filtered to collect a yellow solid which was washed with water and dried under vacuum. This product was stirred with 500 mL of ether and filtered, and the filtrate was evaporated to dryness leaving 2-amino-4,5-dinitrotoluene that was about 86% pure. Two recrystallizations from absolute ethanol gave 39.8 g (45.3%) of **2-amino-4,5-dinitrotoluene** (**4**); mp 190 °C (lit.<sup>2</sup> 191–191.5 °C). The ether-insoluble material from the above reaction was added to 400 mL of 50% sulfuric acid and the mixture stirred at 80 °C for 3 h. The mixture was cooled to 20 °C and filtered, and the yellow product was washed with water and dried under vacuum. Two recrystallizations from absolute ethanol gave 22.8 g (26%) of **2-amino-3,4-dinitrotoluene** (**1**); mp 130–131 °C (lit.<sup>2</sup> mp 131–131.5 °C).

**2-Amino-3,6-dinitrotoluene** (**3**) and **6-Amino-2,3-dinitrotoluene** (**6**). To a nitrating solution (prepared from 260 mL of 96% sulfuric acid and 162 mL of 90% nitric acid) cooled to 5 °C was added, in small portions during 20 min, 60 g of 2-methyl-3-nitroacetanilide, maintaining the temperature at 4–7 °C. After addition was complete the temperature was allowed to rise to 15 °C, at which point the reaction was quenched on 1500 mL of crushed ice. The cream-colored product was filtered, washed thoroughly with water, and dried under vacuum to yield 70.0 g (95%) of a crude product mixture containing 2-acetamido-3,6-dinitrotoluene (**29**) and 6-acetamido-2,3-dinitrotoluene (**30**) (ca. 1:1 ratio by GC/MS assay). To this product mixture was added 450 mL of 50% sulfuric acid, after which the mixture was stirred for 15 min at 25 °C and filtered and the yellow product was washed with water and dried under vacuum. This product was stirred with 250 mL of ether and filtered, and the filtrate was evaporated to dryness leaving 6-amino-2,3-dinitrotoluene that was about 90% pure. Recrystallization from absolute ethanol gave 19.6 g (35%) of pure **6-amino-2,3-dinitrotoluene** (**6**); mp 222 °C (lit.<sup>29</sup> mp 216 °C). The ether-insoluble material above, which contained mainly 2-acetamido-3,6-dinitrotoluene (**29**), was placed in 300 mL of 50% sulfuric acid and the mixture was heated, with stirring at 80–90 °C for 3 h. The mixture was cooled and filtered, and the yellow product was washed with water and dried under vacuum. Recrystallization from absolute ethanol gave 17.4 g (31%) of **2-amino-3,6-dinitrotoluene** (**3**); mp 149–150 °C (lit.<sup>7,9,29</sup> mp 151 °C).

**5-Amino-2,4-dinitrotoluene** (**12**). A mixture of 10.0 g of 2,4-dinitrotoluene and 10.0 g of hydroxylamine hydrochloride in 220 mL of 95% ethanol was cooled to 5 °C and 100 mL of a cool (5 °C) solution of saturated methanolic KOH was added dropwise during 90 min. The solution changed from colorless to blue to brown as the KOH solution was added. After addition of the KOH solution was complete the mixture was stirred at 10 °C for 30 min; 1500 mL of cold water was then added. The resulting mixture was allowed to stand for 1 h and then filtered to yield 3.77 g of nearly pure **12** as a yellow solid (dried over P<sub>2</sub>O<sub>5</sub>). Recrystallization from absolute ethanol yielded 2.41 g (22%) of pure **12**; mp 197–198 °C (lit.<sup>24</sup> mp 196.5–197.5 °C).

**2,5-Dinitro-3-methylbenzoic Acid** (**34**). 7-Methyl-5-nitrosatin (**32**) was prepared by the procedure of Cassebaum<sup>49</sup> from 61 g of 2-methylisonitrosoacetanilide to yield 56.8 g (81%) of **32** as orange crystals; mp 250–255 °C dec (lit.<sup>49</sup> mp 248–249 °C). Compound **32** was converted to 2-amino-3-methyl-5-nitrobenzoic acid (**33**) by Cassebaum's procedure<sup>49</sup> to yield 51.0 g (96%) of **33** as a yellow powder; mp 260–263 °C (lit.<sup>49</sup> mp 265–268 °C (crude), 268 °C (recrystallized from HOAc)).

To trifluoroacetic acid (100 mL) chilled in an ice bath (2 °C), was added, with stirring, 3.3 mL (0.13 mol) of hydrogen peroxide (98% assay). With continued stirring 20.3 mL (0.144 mol) of

trifluoroacetic anhydride was added during 0.5 h keeping the temperature at 2–3 °C. To the resulting solution was added 6.53 g (0.033 mol) of 2-amino-3-methyl-5-nitrobenzoic acid (**33**) during 5 min. A reflux condenser was attached to the flask and the ice bath was removed allowing the solution to warm spontaneously to 42 °C within 20 min. The reaction mixture was then heated under reflux for 3 h. The deep orange solution was concentrated to dryness under reduced pressure and the residue triturated with 100 mL of water. The insoluble product was removed by filtration, washed with water, and dried to yield 5.64 g (75%) of **34**; mp 170–177 °C. Two recrystallizations from aqueous methanol (90% methanol) gave straw-colored prisms: mp 180–181 °C (61.5% recovery); IR (KBr) 1730 (C=O) cm<sup>-1</sup>.

Anal. Calcd for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>: C, 42.49; H, 2.67; N, 12.39; mol wt 226.14. Found: C, 42.68; H, 2.69; N, 12.37; mol wt 230 (vapor osmometry, chloroform).

**3-Amino-2,5-dinitrotoluene** (**8**). 2,5-Dinitro-3-methylbenzoic acid (**34**, 2.43 g, 0.0108 mol) was dissolved in 21.5 g of oleum (20% SO<sub>3</sub>, 80% H<sub>2</sub>SO<sub>4</sub>). While the solution was stirred and the temperature was kept at 5–10 °C by ice-bath cooling, powdered sodium azide (0.84 g, 0.013 mol) was added cautiously in portions of less than 0.1 g during 1 h. **Caution! If the sodium azide is added too rapidly an explosion may result.** Stirring was continued at 0–10 °C for 1 h (gas evolution occurs), 10–30 °C for 2 h, and 30–60 °C for 3 h. The dark mixture was then poured onto 200 mL of crushed ice to yield a yellow-orange precipitate which was removed by filtration, washed with water, and dried to yield 2.02 g (95%) of **8**; mp 125–127 °C. Recrystallization from 95% ethanol gave rust-colored flakes: mp 127–128 °C (79% recovery); IR (KBr) 3400, 3250 (NH<sub>2</sub>) cm<sup>-1</sup>.

Anal. Calcd for C<sub>7</sub>H<sub>7</sub>N<sub>3</sub>O<sub>4</sub>: C, 42.64; H, 3.58; N, 21.32; mol wt 197.15. Found: C, 42.71; H, 3.62; N, 21.33; mol wt 198 (osmometry, chloroform).

**2-Diazo-4,6-dinitro-3-methylphenol** (**37**). 2-Methyl-5-nitroaniline (**35**, 15.2 g, 0.10 mol, mp 107–109 °C) was dissolved in 120 mL of concentrated sulfuric acid with stirring and cooling to 0 °C. Fuming nitric acid (90% HNO<sub>3</sub>, *d* = 1.5; 15 mL, 0.32 mol) was added dropwise with stirring during 15 min while the temperature was maintained at 0 °C. The temperature of reaction mixture was allowed to rise with continued stirring during 3 h (final temperature 30 °C). It was then poured onto 1200 mL of crushed ice and allowed to stand overnight. The gummy, oily product was filtered and triturated with ethanol to yield a dark orange solid which was crystallized from acetic acid to yield 2.57 g (11.5%) of **37**; mp 152–154 °C (vigorous decomposition, followed by an explosion); impact sensitivity (2.5-kg weight) less than 10 cm; IR (Nujol) 2200 (C=N<sub>2</sub>), 1630 cm<sup>-1</sup> (NH bands absent); NMR [(CD<sub>3</sub>)<sub>2</sub>C=O] δ 6.78 (s, 1, ring CH), 2.70 (s, 3, CH<sub>3</sub>); mol wt (mass spectrometry) 224 (parent peak), mol wt calculated for C<sub>7</sub>H<sub>4</sub>N<sub>4</sub>O<sub>5</sub> 224.13.

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**Registry No.** 1, 3484-29-5; 2, 7477-94-3; 3, 56207-39-7; 4, 70343-04-3; 5, 35572-78-2; 6, 70343-05-4; 7, 70343-06-5; 8, 65321-68-8; 9, 10202-92-3; 10, 70343-07-6; 11, 70343-08-7; 12, 5267-27-6; 13, 70343-09-8; 14, 70343-10-1; 15, 19406-51-0; 15 HCl, 70343-11-2; 16, 6393-42-6; 17, 118-96-7; 19, 602-29-9; 24, 59283-75-9; 25, 59283-76-0; 27, 3484-28-4; 28, 70343-12-3; 29, 56207-38-6; 30, 56207-37-5; 32, 70343-13-4; 33, 70343-14-5; 34, 70343-15-6; 35, 99-55-8; 37, 70343-16-7; 2,4,5-trinitrotoluene, 610-25-3; 3,4,5-trinitrotoluene, 603-15-6; 2-methyl-5-nitroacetanilide, 2879-79-0; 2-methyl-3-nitroacetanilide, 56207-36-4; 2,4-dinitrotoluene, 121-14-2; 2-methylisonitrosoacetanilide, 1132-03-2; 2,3,6-trinitrotoluene, 18292-97-2.