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Direct Amination of 1-Substituted 3,5-Dinitrobenzenes by 1,1,1-Trimethylhydrazinium Iodide

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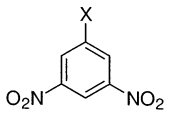
Received December 18, 2000

Abstract: The amination of 1-X-3,5-dinitrobenzenes via the vicarious nucleophilic substitution of hydrogen (VNS) with 1,1,1-trimethylhydrazinium iodide (TMHI) in the presence of *t*-BuOK or NaOMe in DMSO was studied. It was observed (when X = OMe, OCH_2CF_3, $OCH_2CF_2CF_2H$, OPh) that the amination occurs regioselectively (ratio of *ortho*/*para*-isomers is ~9:1) and with high yield. For X = SPh or SCH_2Ph, the reaction proceeded with a low yield (less than 20%), with a ratio of ortho/para-isomers ≈ 1:1. For X = $PhSO_2$ and 2 equiv of TMHI, a double amination occurs and 2,4-diamino-3,5-dinitro-1-phenylsulfonylbenzene predominates in the mixture of isomers. Under the same conditions, 1,3,5-trinitrobenzene undergoes a double amination to yield 2,4-diamino-1,3,5-trinitrobenzene. A proposed mechanism for this reaction is discussed.

Previously, conditions were found under which a nitro group in 1,3,5-trinitrobenzene, when acted upon by phenols,[1,2] thiols,[3,4] and polyfluorinated alcohols,[5−7] undergoes substitution to give corresponding 1-X-3,5-dinitrobenzenes (**1**). Thus, preparative methods for the synthesis of previously unknown compounds of type **1** were elaborated. In this paper, we report the results of our studies on the amination of compounds **1** by means of vicarious nucleophilic substitution (VNS) of hydrogen.[8,9] The present work comprises one part of a systematic investigation directed toward a search for new methods of chemical utilization of aromatic explosives.



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X = ArO−, CF_3CH_2O−, $CHF_2CF_2CH_2O$−, $RS(O)_n$− (n = 0,1,2; R = alkenyl, Ar)

The direct amination of substituted mononitrobenzenes by VNS reagents is known. The efficiency and regioselectivity of amination as a function of the aminating agent and the reaction conditions have been studied.[10−14] However, there are only two reported examples of VNS amination of a 1-X-3,5-dinitrobenzene compound. For 1,3-dinitrobenzene (X = H), VNS amination gives either the disubstituted product, 1,3-diamino-2,4-dinitrobenzene, or a mixture of the latter with the product of monoamination, 2,4-dinitroaniline,[10,14] depending on the amount and type of VNS reagent used and reaction conditions. The other example is 1,3,5-trinitrobenzene (X = NO_2) which, when treated with hydroxylamine under basic conditions, gives picramide with a small amount of disubstituted product, 1,3-diamino-2,4,6-trinitrobenzene.[10]

For the amination of 1,3-dinitrobenzenes **1**, we have employed 1,1,1-trimethylhydrazinium iodide (TMHI), which is a highly efficient VNS aminating reagent with respect to mononitrobenzenes, 1,3-dinitrobenzene, and picramide.[14−16] This reagent was obtained by quaternization of commercially available 1,1-dimethylhydrazine with methyl iodide. We have chosen for amination those compounds of type **1** that have substituents X possessing considerably different electronic and steric properties along with 3,5-dinitroanisole[17] (**1a**, X = OMe) and trinitrobenzene (**1h**, X = NO_2).

Dinitrobenzenes **1a**−**f** undergo amination by TMHI under previously reported conditions[14] giving the corresponding dinitroanilines **2/3a**−**f** (Scheme 1) in the form of *ortho*/*para*-isomers (**2**/**3**) relative to functional group X.

In all cases except thio-substituted dinitrobenzenes **1e**,**f**, we obtained dinitroanilines **2/3** in excellent yields and with a significant predominance of *ortho*-isomers

(1) Shevelev, S. A.; Dutov, M. D.; Vatsadze, I. A.; Serushkina, O. V.; Rusanov, A. L.; Andrievskii, A. M. *Mendeleev Commun.* **1995**, 157.
(2) Shevelev, S. A.; Dutov, M. D.; Vatsadze, I. A.; Serushkina, O. V.; Korolev, M. A.; Rusanov, A. L. *Russ. Chem. Bull.* **1995**, *44*, 384.
(3) Shevelev, S. A.; Dutov, M. D.; Serushkina, O. V. *Russ. Chem. Bull.* **1995**, *44*, 2424.
(4) Shevelev, S. A.; Dutov, M. D.; Serushkina, O. V.; Sapozhnikov, O. Yu. 18th International Symposium on the Organic Chemistry of Sulfur, Florence, Italy, July 13−18, 1998; Book of Abstracts 1998, p 189.
(5) Shevelev, S. A.; Dutov, M. D.; Korolev, M. A.; Sapozhnikov, O. Yu.; Rusanov, A. L. *Mendeleev Commun.* **1998**, 69.
(6) Shevelev, S. A.; Dutov, M. D.; Korolev, M. A.; Sapozhnikov, O. Yu.; Rusanov, A. L. *Russ. Chem. Bull.* **1998**, *47*, 1623.
(7) Shevelev, S. A.; Dutov, M. D.; Korolev, M. A.; Sapozhnikov, O. Yu.; Rusanov, A. L., Komarova, L. G., Prigozhina, M. P., Askadsky, A. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 851.
(8) Makosza, M.; Winiarski, J. *Acc. Chem. Res.* **1987**, *20*, 282.
(9) Makosza, M.; Wojciechowski, K. *Liebigs Ann. Chem.* **1997**, 1805.
(10) Meisenheimer, J.; Patzig, E. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 2533.
(11) Katrizky, A.; Laurenzo, K. *J. Org. Chem.* **1986**, *51*, 5040.
(12) Makosza, M.; Bialecki, M.*J. Org. Chem.* **1992**, *57*, 4784. Makosza, M.; Bialecki, M. *J. Org. Chem.* **1998**, *63*, 4878.
(13) Seko, S.; Kawamura, N. *J. Org. Chem.* **1996**, *61*, 442. Seko, S.; Miyake, K.; Kawamura, N. *Perkin Trans. 1* **1999**, 1437.
(14) Pagoria, P. F.; Mitchell, A. R.; Schmidt, R. D. *J. Org. Chem.* **1996**, *61*, 2934.
(15) Mitchell, A. R.; Pagoria, P. F.; Schmidt, R. D. U.S. Patent 5 569 783, 1996; *Chem. Abstr.* **1997**, *126*, 77037.
(16) Mitchell, A. R.; Pagoria, P. F.; Schmidt, R. D. U.S. Patent 6 069 277, 2000.
(17) Izzo, P. T. *J. Org. Chem.* **1959**, *24*, 2026.

10.1021/jo005774c CCC: $25.00
Published on Web 02/15/2003

SCHEME 1

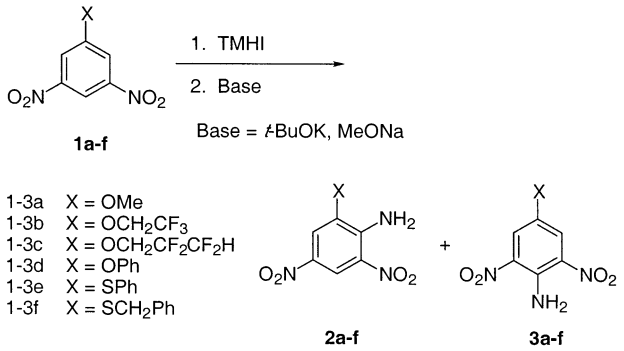


TABLE 1. Results of VNS Amination of Compounds 1a−h with TMHI

starting compd	products		yield (%)	ratio of isomers (*o*/*p*)
1a	**2a**	**3a**	90[a]	90:10
1b	**2b**	**3b**	91[a]	95:5
1c	**2c**	**3c**	87[a]	98:2
1d	**2d**	**3d**	90[a]	90:10
1e	**2e**	**3e**	23	55:45
1f	**2f**	**3f**	15	55:45
1g[b]	**4**	**5**	92[a]	90:10
1h[b]	**6**	**86**		

[a] Yield of the mixture of isomers. [b] Reaction with 2 equiv of TMHI.

(Table 1). In the case of dinitrobenzenes **1e**,**f**, significant amounts of tar were produced during the reaction, presumably due to the instability of the products **2/3e**,**f** under strongly basic conditions. This hypothesis was checked by exposing **2/3e**,**f** to a solution of *t*-BuOK in DMSO, which after standing overnight, resulted in the production of a dark polymeric material. Thus, **2/3e**,**f** were isolated in lower yields during the basic amination reaction.

While the reaction proceeded faster when *t*-BuOK was used as the base, both *t*-BuOK and MeONa were tried with no significant effect on product yields. In the case of dinitrobenzenes **1a**−**f**, it should be emphasized that, although an excess of TMHI was used, the only reaction product was the monoamine: the formation of a diamine was never detected.

Sulfone **1g** appeared to be more reactive than the corresponding dinitrobenzenes (**1a**−**f**), and when 2 equiv of TMHI was used, the result was formation of diamines **4** and **5** (Scheme 2). The yield of the isomeric mixture was 92%, and two isomers **4** and **5** were formed in a 9:1 ratio (Table 1). On the other hand, if only 1 equiv of TMHI was used in the reaction, then another mixture of products was formed: the starting sulfone (**1g**), diamine **4**, and monoamine **2g** in a ratio of 5:4:1. When 1,3,5-trinitrobenzene (**1h**), which is analogous to sulfone **1g** with respect to the electronic effect of its substituents, was acted upon by to 2 equiv of TMHI, it was converted to the product of double amination, 2,4-diamino-1,3,5-trinitrobenzene (**6**) (Scheme 2).

It is believed that the amination of 1-X-3,5-dinitrobenzenes proceeds in accordance with the VNS mechanism[11,12,19] (Scheme 3).

In the presence of a strong base, deprotonation of TMHI occurs, resulting in the formation of trimethylammonium imide (TMAI). The latter adds to the aromatic ring of 1-X-3,5-dinitrobenzene (**1**) in either the *ortho*- or *para*-position relative to X to give the corresponding σ-adducts. When the σ-adducts are acted upon by a base, deprotonation with simultaneous elimination of trimethylamine takes place. After acidification, isomeric products **2** and **3** are formed. The substantial predominance of *ortho*-isomers in the case of amination of **1a**−**d** is presumably connected with the thermodynamic stability of the σ-complex. In fact, it might be expected that the addition of the nucleophile to the *ortho*-position relative to X will give a more stable complex than in the case of that to the *para*-position, since in the former the negative charge is more efficiently delocalized.[20] In the case of sulfur-containing 1,3-dinitrobenzenes **1e**,**f**, overall yields of the corresponding dinitroanilines were low. Since different rates of isomer decomposition are possible, this may account for the significant variances in the ratio of *ortho*/*para*-isomers in these instances.

Experimental Section

General Methods. Most NMR spectra were recorded on a 400 MHz spectrometer (operating at 400.13 MHz for ^{1}H, 376.48 MHz for ^{19}F, and 100 MHz for ^{13}C). For compounds **2e**,**f** and **3e**,**f**, ^{13}C NMR spectra were recorded on a 500 MHz spectrometer (operating at 125.77 MHz). Chemical shifts are expressed in parts per million downfield of tetramethylsilane internal standard for ^{1}H and ^{13}C and relative to the CF_3CO_2H external standard for ^{19}F. Starting materials were prepared according to literature procedures as follows: dinitroanisole (**1a**),[17] fluoroalkoxydinitrobenzenes (**1b**,**c**),[5,6] 3,5-dinitro-1-phenoxybenzene (**1d**) and 3,5-dinitro-1-phenylthio-benzene (**1e**),[1−3] dinitrobenzenes (**1f**−**h**),[21] and 1,1,1-trimethylhydrazinium iodide.[14]

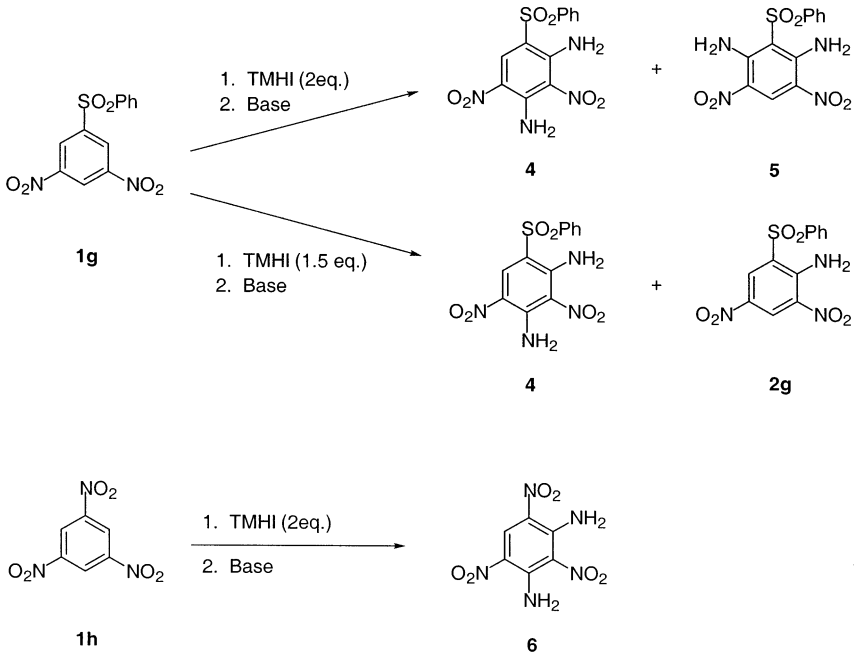
The structures of products **2** and **3** were determined by ^{1}H and ^{13}C NMR spectroscopy and by elemental analysis. Elemental analysis was carried out by the Laboratory of Microanalysis of the N. D. Zelinsky Institute of Organic Chemistry. The ratio of *ortho*/*para*-isomers **2/3** was established by ^{1}H NMR spectroscopy according to the integral intensity of aromatic protons in the ring containing the nitro groups. Diamine **6** was identified by comparison of the isolated product with an authentic sample.[18]

CAUTION! 2,4,6-Trinitrobenzene (TNB) and 2,4-diamino-1,3,5-trinitrobenzene are explosive. It is strongly recommended that they be handled with great care and proper precaution.

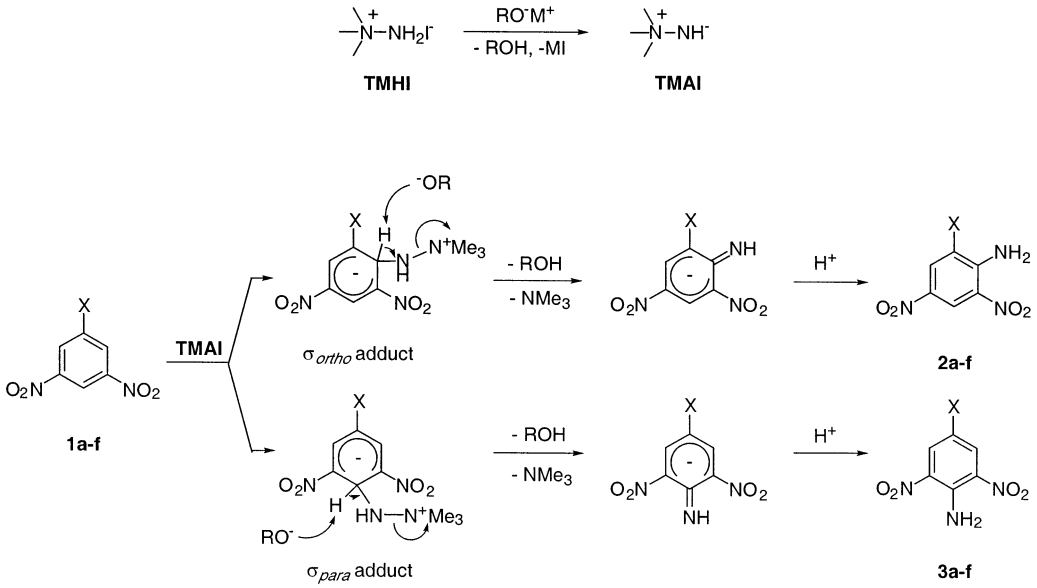
Notes on NMR Spectral Interpretation. Interpretation of the signals of carbon atoms in the ^{13}C NMR spectra of amines **2/3b**,**c** has been performed with regard to chemical shifts of the starting arenes (**1b**,**c**) and by the selective heteronuclear double-resonance technique. If the protons of the OCH_2 group in **2b** and **2c** are decoupled, the splitting of coupling constant $^3J_{COCH_2}$ disappears in the low-field ^{13}C signals (δ 145.6 for **2b** and δ 145.51 for **2c**). The broadband signal of the 1-C carbon atom transforms into the doublet of triplets with the coupling constants $^2J_{1-C,\ 6-CH}$ and $^3J_{1-C,\ 2-CNH_2}$. In compound **2d**, the interpretation of the signals for carbon atoms 1-C and 1′-C has been performed with regard to their multiplicity as well as with the use of the selective heteronuclear double-resonance technique. When the protons of the NH_2 group are decoupled, the broadband multiplet of the 1-C carbon atom (δ 146.25) becomes a doublet with $^2J_{1-C,\ 6-CH}$ coupling constant. The other carbon signals were interpreted in view of chemical shifts in compounds **2b** and **2c**.

(18) Warman, M.; Siele, V. I., *J. Org. Chem.* **1961**, *26*, 2997.
(19) Makosza, M.; Glinka, T. *J. Org. Chem.* **1983**, *48*, 3860.
(20) Terrier, F. *Chem. Rev.* **1982**, *82*, 77.
(21) Dutov, M. D.; Serushkina, O. V.; Shevelev, S. A. *Russ. Chem. Bull.* **2001**, *50*, 261.

SCHEME 2



SCHEME 3



General Amination Method (Typical Procedures): Reaction of 1a−f. To a solution of 0.3 g (1.12 mmol, 1 equiv) of dinitro compound **1b** and 0.34 g (1.68 mmol, 1.5 equiv) of TMHI in 15 mL of anhydrous DMSO was added solid *t*-BuOK (0.38 g, 3.36 mmol, 3 equiv), and the reaction mixture was stirred at room temperature until the starting material was completely reacted, as indicated by TLC monitoring (2−2.5 h). The resulting dark red solution was poured into a mixture of 50 g of ice and 25 mL of concentrated HCl_{aq}. The compounds **2/3a** and **2/3c−f** were obtained in the same manner.

Products 2/3a−d. The precipitated crystals were recovered by suction filtration and recrystallized from 2:1 MeCN−H_2O. In the case of products **2/3e**,**f**, the resulting tar was dissolved in acetone, and the products were separated using column chromatography (silica gel, 4:1 petroleum ether−acetone).

Reaction of 1g−h. To a solution of 0.3 g (0.97 mmol) of sulfone **1g** or 0.3 g (1.4 mmol) of 2,4,6-trinitrobenzene **1h** and 0.39 g (1.93 mmol) of TMHI (0.57 g (2.8 mmol) of TMHI was used for **1h**) in 15 mL of anhydrous DMSO was added solid *t*-BuOK (0.33 g (2.94 mmol) for **1g** or 0.47 g (4.2 mmol) for **1h**), and the reaction mixture was stirred at room temperature for 2 h. The resulting solution was poured into a mixture of 50 g of ice and 25 mL of concentrated HCl_{aq}. Products were collected by filtration and recrystallized from MeCN.

2-Amino-1-methoxy-3,5-dinitro- and 4-Amino-1-methoxy-3,5-dinitrobenzenes (2/3a). 2a: yield 70%, mp 178 °C (lit.[22] 176 °C); ^{1}H NMR (acetone-d_6) δ 4.23 (s, 3H), 8.02 (br, 2H), 7.99 and 8.71 (d, ^4J = 2.4 Hz, 2H). **3a:** ^{1}H NMR (acetone-d_6) δ 4.12 (s, 3H), 7.95 (s, 2H).

2-Amino-1-(2,2,2-trifluoroethoxy)-3,5-dinitro- and 4-Amino-1-(2,2,2-trifluoroethoxy)-3,5-dinitrobenzenes (2/3b). 2b: yield 72%, mp 137−138 °C; ^{1}H NMR (acetone-d_6) δ 5.08 (q, $^3J_{HF}$ = 8.5 Hz, 2H), 8.02 (br, 2H), 8.02 d and 8.74 (d, ^4J = 2.4 Hz,

(22) Horner, L.; Shwenk, U., Junghanns, E. *Liebigs Ann. Chem.* **1953**, *579*, 212.

2H); ^{19}F NMR (acetone-d_6) δ 6.98 (t, $^3J_{HF}$ = 8.5 Hz); ^{13}C NMR (DMSO-d_6) δ 66.12 (qt, ^1J = 151.1 Hz, $^2J_{CF}$ = 34.9 Hz), 109.51 (dd, ^1J = 167.1 Hz, ^3J = 5.8 Hz), 116.58 (dd, ^1J = 172.9 Hz, ^3J = 4.4 Hz), 123.4 (qt, $^1J_{CF}$ = 277.6 Hz, $^2J_{CH}$ = 4.4 Hz), 126.8 (m, J = 4.4 Hz, J = 1.5 Hz), 133.8 (dd, J = 4.4 Hz, J = 5.8 Hz), 141.76 (dd, J = 4.4 Hz, J = 5.8 Hz), 145.46 (m, J = 4.4 Hz, J = 5.8 Hz). **3b:** ^{1}H NMR (acetone-d_6) δ 4.89 (q, $^3J_{HF}$ = 8.5 Hz, 2H), 7.97 (s, 2H). Anal. Calcd for $C_8H_6F_3N_3O_5$: C, 34.18; H, 2.15; N, 14.95. Found: C, 34.23; H, 2.21; N, 14.92.

2-Amino-1-(2,2,3,3-tetrafluoropropoxy)-3,5-dinitro- and 4-Amino-1-(2,2,3,3-tetrafluoropropoxy)-3,5-dinitrobenzenes (2/3c). 2c: yield 68%, mp 164−165 °C; ^{1}H NMR (acetone-d_6) δ 4.98 (tt, ^3J = 12.4 Hz, ^4J = 1.4 Hz, 2H), 6.73 (tt, ^2J = 52.3 Hz, ^3J = 5.4 Hz, 1H), 7.82 (br s, 2H), 8.02 and 8.72 (d, ^4J = 2.7 Hz, 2H); ^{19}F NMR (acetone-d_6) δ 59.7 (ddt, $^2J_{HF}$ = 53.3 Hz, $^3J_{FF}$ = 4.9 Hz, $^3J_{HF}$ = 1.3 Hz), 45.10 (ttd, $^3J_{HF}$ = 12.4 Hz, $^3J_{HF}$ = 5.5 Hz, $^3J_{FF}$ = 4.9 Hz); ^{13}C NMR (DMSO-d_6) δ 66.12 (qt, $^1J_{CH}$ = 151.1 Hz, $^2J_{CF}$ = 34.9 Hz), 108.9 (dtt, ^1J = 215.1 Hz, ^1J = 247.1 Hz, ^2J = 32.0 Hz), 109.02 (dd, ^1J = 168.6 Hz, ^3J = 5.8 Hz), 114.65 (ttm, ^1J = 248.5 Hz, ^2J = 26.2 Hz, ^3J = 4.4 Hz), 116.41 (dd, ^1J = 172.9 Hz, ^3J = 4.4 Hz), 128.51 (m, J = 4.4 Hz), 133.76 (dd, J = 5.8 Hz, J = 4.4 Hz), 141.58 (dd, J = 5.8 Hz, J = 4.4 Hz), 145.51 (m, J = 5.8 Hz, J = 4.4 Hz). **3c:** ^{1}H NMR (acetone-d_6) δ 5.01 (tt, ^3J = 12.4 Hz, ^4J = 1.4 Hz, 2H), 6.63 (tt, ^2J = 52.3 Hz, ^3J = 5.4 Hz, 1H), 7.95 (s, 2H). Anal. Calcd for $C_9H_7F_4N_3O_5$: C, 34.52; H, 2.25; N, 13.42. Found: C, 34.58; H, 2.21; N, 13.47.

2-Amino-3,5-dinitro-1-phenoxy- and 4-Amino-3,5-dinitro-1-phenoxybenzenes (2/3d). 2d: yield 71%, mp 159−160 °C; ^{1}H NMR ($CDCl_3$) δ 7.11 (m, 2H), 7.31 (m, 1H), 7.48 (m, 2H), 7.64 and 8.88 (d, ^4J = 2.6 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 113.31 (dd, ^1J = 167.1 Hz, ^3J = 5.8 Hz), 117.38 (dd, $^1J_{CH}$ = 172.9 Hz, ^3J = 4.4 Hz), 119.47 (ddd, ^1J = 161.3 Hz, J = 7.3 Hz, J = 2.9 Hz), 125.13 (dtt, ^1J = 162.8 Hz, J = 5.8 Hz, J = 4.4 Hz), 129.25 (dt, J = 4.4 Hz, J = 2.9 Hz), 133.55 (t, J = 4.4 Hz), 142.96 (t, J = 4.4 Hz), 146.25 (m, J = 5.8 Hz, J = 4.4 Hz), 154.71 (tt, J = 5.8 Hz, J = 4.4 Hz). **3d:** ^{1}H NMR ($CDCl_3$) δ 7.03 (m, 2H), 7.2 (m, 1H), 7.39 (m, 2H), 7.91 (s, 2H). Anal. Calcd for $C_{12}H_9N_3O_5$: C, 52.37; H, 3.30; N, 15.27. Found: C, 52.41; H, 3.34; N, 15.25.

2-Amino-3,5-dinitro-1-phenylthio- and 4-Amino-3,5-dinitro-1-phenylthiobenzenes (2/3e). 2e: mp 136−138 °C; ^{1}H NMR (acetone-d_6) δ 7.28−7.36 (m, 5H), 8.01 (br s, 2H), 8.57 and 9.05 (d, ^4J = 2.7 Hz, 2H); ^{13}C NMR (acetone-d_6) δ 105.61, 124.34, 128.05, 128.30, 130.20, 130.95, 136.68, 138.10, 143.46, 148.69, **3e**: mp 203−205 °C; ^{1}H NMR (acetone-d_6) δ 7.28−7.36 (m, 5H), 8.65 (s, 2H), 9.54 (br s, 2H).); ^{13}C NMR (acetone-d_6) δ 125.97, 126.45, 129.03, 130.22, 131.22, 138.06. Anal. Calcd for $C_{12}H_9N_3O_4S$: C, 49.48; H, 3.11; N, 14.43. Found: C, 49.51; H, 3.13; N, 14.45.

2-Amino-1-benzylthio-3,5-dinitro- and 4-Amino-1-benzylthio-3,5-dinitrobenzenes (2/3f). 2f: mp 117−118 °C; ^{1}H NMR (acetone-d_6) δ 4.14 (s, 2H), 7.24 (m, 5H), 8.03 (br s, 2H), 8.15 and 8.92 (d, ^4J = 2.7 Hz, 2H); ^{13}C NMR (acetone-d_6) δ 40.33, 124.6, 125.09, 129.09, 130.05, 130.72, 132.8, 136.8, 137.30, 138.45, 150.7 **3f**: mp 110−114 °C; ^{1}H NMR (acetone-d_6) δ 3.99 (s, 2H), 7.24 (m, 5H), 8.14 (s, 2H), 9.47 (br s, 2H); ^{13}C NMR (acetone-d_6) δ 40.33, 125.09, 129.09, 130.05, 130.72, 137.31, 138.45. Anal. Calcd for $C_{13}H_{11}N_3O_4S$: C, 51.14; H, 3.63; N, 13.76. Found: C, 51.13; H, 3.64; N, 13.77.

2,6-Diamino-3,5-dinitro-1-phenylsulfonyl- and 2,4-Diamino-3,5-dinitro-1-phenylsulfonyl-benzenes (4/5). 4: yield 60%, mp 262−264 °C; ^{1}H NMR (DMSO-d_6) δ 7.63 (m, 2H), 7.75 (m, 1H), 8.03 (m, 2H), 8.17 (br s, 2H), 8.83 (s, 1H), 9.06 (br s, 2H); ^{13}C NMR (DMSO-d_6) δ 110.49 (m, J = 5.8 Hz), 120.88 (m, J = 4.4 Hz), 122.62 (m, J = 5.8 Hz), 126.64 (dt, ^1J = 165.6 Hz, J =5.8 Hz), 129.52 (dd, ^1J = 165.6 Hz, J = 7.3 Hz), 133.89 (dt, ^1J = 164.2 Hz, J = 7.3 Hz), 134.93 (d, ^1J = 168.8 Hz), 140.04 (t, J = 8.7 Hz), 146.29 (d, J = 5.8 Hz), 147.56 (d, J = 8.7 Hz). **5:** ^{1}H NMR (acetone-d_6) δ 7.66 (m, 2H), 7.74 (m, 1H), 8.06 (m, 2H), 9.06 (s, 1H), 9.51 (br s, 2H). Anal. Calcd for $C_{12}H_{10}N_4O_6S$: C, 42.60; H, 2.98; N, 16.56. Found: C, 42.58; H, 3.02; N, 16.57.

2-Amino-3,5-dinitro-1-phenylsulfonylbenzene (2g). ^{1}H NMR (acetone-d_6) δ 7.66 (m, 2H), 7.75 (m, 1H), 8.03 (m, 2H), 8.12 and 8.65 (d, ^4J = 2.7 Hz, 2H).

Acknowledgment. This work has been supported by the International Science and Technology Center (Project 419-98) (V.V.R., S.A.S., and I.I.C.). The work at Livermore (A.R.M. and R.D.S.) was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

JO005774C