Improved Synthesis of 3,5-Diamino-2,4,6-trinitrotoluene

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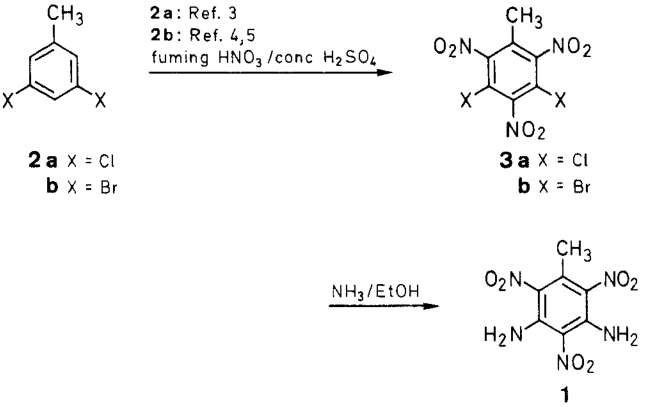
A three step, efficient synthesis is described that provides the title compound in 58% overall yield from orcinol (3,5-dihydroxytoluene) monohydrate.

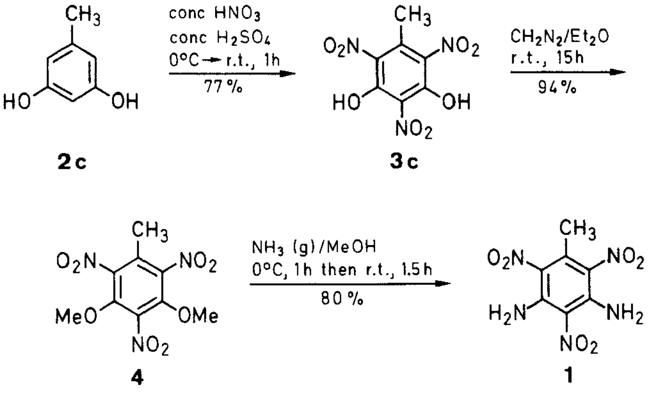
Polynitroaromatic compounds constitute an important class of high density energetic materials that are utilized as explosives. Polynitroaromatic compounds that contain an α-C−H group (e.g., 2,4,6-trinitrotoluene, TNT) consistently show greater impact sensitivity than similar compounds that contain the same oxygen balance but do not possess the α-C−H functionality.[1] It has been demonstrated that the impact sensitivity of polynitrotoluenes can be reduced significantly by the introduction of one or more amino groups.[2] 3,5-Diamino-2,4,6-trinitrotoluene (DATNT, **1**) is of particular interest in this connection, as this compound is proposed to be a more powerful explosive than TNT but is less impact-sensitive.[3]

Compound **1** has been synthesized previously in two steps by starting either with 3,5-dichloro-[3] or 3,5-dibromotoluene[4,5] (**2a** or **2b**, respectively). These syntheses suffer from the following limitations: (i) One of the starting materials, **2a**, is not available commercially; the other is available and can be purchased, but it is very expensive. (ii) Due to the cumulative ring-deactivating influence of the halogen substituents, harsh conditions (e.g., fuming HNO_3/concentrated H_2SO_4) are required to effect trinitration of **2a** and of **2b**. (iii) The reaction of **3b** with ethanolic ammonia has been reported[4] to require elevated pressure; thus, this reaction must be performed in a sealed reaction vessel.



More recently, Atkins and co-workers[6] have reported that **1** can be synthesized by reacting either pentanitrotoluene or 3-amino-2,4,5,6-tetranitrotoluene with ammonia in dioxane at ambient temperature and atmospheric pressure. However, these procedures both employ starting materials that are powerful explosives which are not readily available and must be prepared via multistep synthesis.

In an effort to overcome the limitations described above, we have developed a simple and convenient three-step procedure that affords **1** in 58% overall yield. Our procedure employs as starting material 3,5-dihydroxytoluene (orcinol, **2c**), which is both commercially available (as the monohydrate) and relatively inexpensive.



The hydroxy groups in **2c** activate the aromatic ring toward electrophilic nitration. Thus, trinitration of this material is performed conveniently and in high yield (77%) simply by using concentrated HNO_3/concentrated H_2SO_4.[7] *O*-Methylation of the hydroxy groups in the trinitration product, **3c**, is carried out in high yield (94%) by using ethereal diazomethane.[8,9] Finally, nucleophilic aromatic substitution of the methoxy groups in **4** is executed conveniently and in high yield (80%) by reacting a methanol solution of this compound with ammonia gas under ambient conditions.

In summary, our three-step synthesis of **1**, described above, offers the following advantages:

- each synthetic step is easy to set up, to perform, and to work up;
- only inexpensive and readily available reagents are required;
- mild conditions are utilized for the trinitration step;
- handling of polynitroaromatics is minimized, and our procedure does not subject them to harsh environmental conditions;
- the use of elevated pressure in the amination step is avoided; and
- the desired material is produced in high overall yield.

We anticipate that this procedure will lend itself readily to scaleup and thus may find application for large scale synthesis of **1**.

Melting points are uncorrected. *WARNING!* Polynitroaromatics are powerful explosives and should be handled with extreme caution.

3,5-Dihydroxy-2,4,6-trinitrotoluene (3c):
A solution of orcinol monohydrate (**2c**, 284 mg, 2.0 mmol) in conc H_2SO_4 (15 mL) was cooled externally (ice-water bath) to 0°C. A

precooled (0 °C) mixture of conc HNO_3 (0.8 mL) and conc H_2SO_4 (1.6 mL) was added dropwise with stirring to the reaction vessel. This was followed by dropwise addition of cold, conc. HNO_3 (1.5 mL) to the stirred mixture. The external cold bath was removed, and the mixture was allowed to warm gradually to r.t. during 1 h. The mixture then was poured into ice-water (25 mL). The product, which precipitated immediately, was isolated via suction filtration and air-dried. Pure **3c** (398 mg, 77 %) was thereby obtained as a yellow-orange microcrystalline solid; mp 166–168 °C (lit. mp 171–172 °C[7]; 162 °C[10]).

IR (Nujol): ν = 3160 (s), 1628 (m), 1592 (s), 1541 (s), 1469 (s), 1375 (s), 1188 cm^{-1} (s).

^1H NMR (acetone-d_6): δ = 2.36 (s, 3 H), 10.06 (br s, 2 H).

^{13}C NMR (acetone-d_6): δ = 14.02 (q), 125.77 (s), 133.64 (s), 134.99 (s), 149.75 (s).

3,5-Dimethoxy-2,4,6-trinitrotoluene (4):

A solution of diazomethane in Et_2O was added dropwise with stirring to a solution of **3c** (130 mg, 0.50 mmol) in EtOAc (10 mL).[8] The addition was continued until the yellow color of diazomethane persisted, thereby indicating the presence of a slight excess of this reagent. The resulting solution was stirred overnight (15 h) at r.t. and was then concentrated in vacuo. Pure **4** (135 mg, 94 %) was thereby obtained as a yellow microcrystalline solid; mp 66–67 °C (lit.[8] mp 65–66 °C).

IR (Nujol): ν = 1592 (s), 1538 (s), 1466 (s), 1365 (s), 1136 cm^{-1} (s).

^1H NMR ($CDCl_3$): δ = 13.25 (q), 64.56 (q), 127.63 (s), 138.55 (s), 141.54 (s), 146.19 (s).

3,5-Diamino-2,4,6-trinitrotoluene (1):

A solution of **4** (100 mg, 0.35 mmol) in MeOH (10 mL) under argon was cooled externally (ice-water bath) to 0 °C and was stirred vigorously. Ammonia gas was bubbled continuously through this cooled solution for 1.5 h. The external cold bath was removed, and slow passage of ammonia gas through the mixture was continued with vigorous stirring for an additional 1.5 h. The gas bubbling apparatus was removed, the flask was stoppered, and the mixture was stirred at r.t. for 1.5 h. The stopper was removed, and excess ammonia was allowed to evaporate slowly from the mixture. During this time, compound **1** slowly crystallized from the mixture. The product was collected by suction filtration, and the residue washed with MeOH and then air-dried. Pure **1** (72 mg, 80 %) was thereby obtained as yellow needles; mp 223–224 °C (lit. mp 222 °C,[3] 222.5–224 °C[6]).

IR (Nujol): ν = 3439 (m), 3320 (m), 1585 (m), 1469 (s), 1340 cm^{-1} (m).

^1H NMR ($CDCl_3$): δ = 2.41 (s, 3 H), 8.0–8.3 (br s, 4 H).

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(1) Kamlet, M.J.; Adolph, H.J. *Propellants Explosives* **1979**, *4*, 30.
Wilson, W.S.; Bliss, D.E.; Christian, S.L.; Knight, D.J. *Explosive Properties of Polynitroaromatics*; Naval Weapons Center Technical Publication 7073; April, 1990.
(2) Iyer, S.l. *Propellants, Explosives, Pyrotechnics* **1982**, *7*, 37.
(3) Iyer, S. *J. Energetic Materials* **1984**, *2*, 151.
(4) Palmer, A.W. *Ber. Dtsch. Chem. Ges.* **1889**, *21*, 3501.
(5) Joshi, S.S.; Gupta, S.P. *J. Indian Chem. Soc.* **1959**, *33*, 329.
(6) Atkins, R.L.; Hollins, R.A.; Wilson, W.S. *J. Org. Chem.* **1986**, *51*, 3261.
(7) Birch, A.J.; Massey-Westropp, R.A.; Rickards, R.W.; Smith, H. *J. Chem. Soc.* **1958**, 360.
(8) Rao, K.V.; Kuo, H.-S. *J. Heterocycl. Chem.* **1979**, *16*, 1241.
(9) At the suggestion of two referees, alternative methods to replace the use of diazomethane for *O*-methylation of **3c** were sought, as diazomethane was regarded as being unsuitable for use in large-scale reactions. The following methods were attempted: (a) dimethyl sulphate/acetone/solid K_2CO_3, reflux, 4 h; (b) MeI/HMPT/aq NaOH, 25 °C, stir 6 h; (c) MeI, DMSO/powdered KOH, 25 °C, stir 0.5 h. In each case, decomposition of the starting material resulted; no **4** could be isolated from any of these alternative procedures for performing *O*-methylation of **3c**.
(10) Stenhouse, J. *J. Chem. Soc.* **1871**, 357.