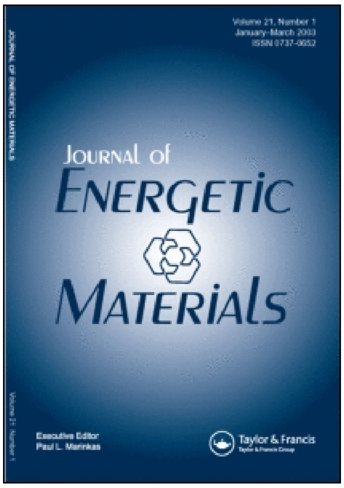


Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Preparation of 1,3,5-triamino-2,4,6-trinitrobenzene from 3,5-dichloroanisole

D. G. Ott[a]; T. M. Benziger[a]
[a] Explosives Technology Group Los Alamos National Laboratory, University of California, Los Alamos, New Mexico, U.S.A.

To cite this Article Ott, D. G. and Benziger, T. M.(1987) 'Preparation of 1,3,5-triamino-2,4,6-trinitrobenzene from 3,5-dichloroanisole', Journal of Energetic Materials, 5: 3, 343 — 354

To link to this Article: DOI: 10.1080/07370658708012359

URL: http://dx.doi.org/10.1080/07370658708012359

PREPARATION OF 1,3,5-TRIAMINO-2,4,6-TRINITROBENZENE FROM 3,5-DICHLOROANISOLE

D. G. Ott and T. M. Benziger

Explosives Technology Group

Los Alamos National Laboratory, University of California

Los Alamos, New Mexico 87545, U.S.A.

ABSTRACT

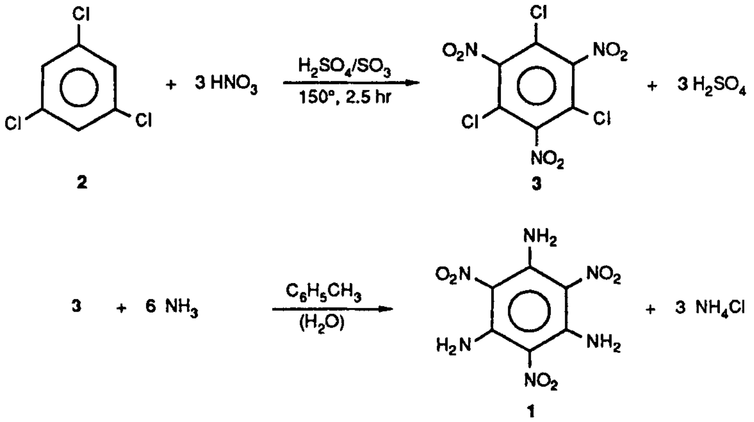
Nitration of 3,5-dichloroanisole under relatively mild conditions gave 3,5-dichloro-2,4,6-trinitroanisole (DCTNA) in high yield and purity. Ammonolysis of the DCTNA afforded 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Treatment of DCTNA with thionyl chloride and dimethylformamide gave 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB). Ammonolysis of TCTNB also produced TATB. Comparisons of these routes with that starting from nitration of 1,3,5-trichlorobenzene have been made.

Journal of Energetic Materials vol. 5, 343-354 (1987)

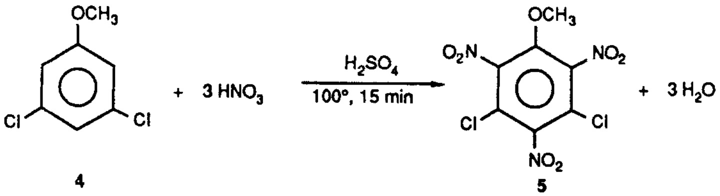
Published in 1987 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

Triaminotrinitrobenzene (TATB, 1) is an explosive with unusual insensitivity, stability at high temperatures, and respectable performance.[1] Extensive examinations of its properties have shown that TATB offers a degree of safety for explosives applications that is unique. Its highly hydrogen-bonded and symmetrical structure[2] is undoubtedly the reason for much of its extraordinary chemical and physical behavior, such as its insolubility in organic solvents and melting point above 400°C. The compound was first synthesized in 1887 from tribromotrinitrobenzene.[3] TATB has also been prepard on a laboratory scale from 2,4,6-trinitrotoluene through selective reduction of the 4-nitro group, nitration to pentanitroaniline, and then ammonolysis.[4] Numerous studies have led to the procedures currently used for the manufacture of TATB on a large scale[1] starting from 1,3,5-trichlorobenzene (TCB, 2). Nitration conditions to give the intermediate 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB, 3) are severe, requiring high temperature, long reaction time, and oleum, and result in formation of a significant amount of by-pro-



duct. The procedures reported here offer two alternative routes to TATB starting from 3,5-dichloroanisole (DCA, 4)--one by direct ammonolysis of 3,5-dichloro-2,4,6-trinitroanisole (DCTNA, 5), and another through its prior conversion to 3. The principal advantages are the ease of nitration of 4, as compared to 2, and the purity of product 5, which is produced rapidly in high yield. Development of a continuous nitration process for production of 5 from 4 (which is not practical for 3 from 2) appears feasible.



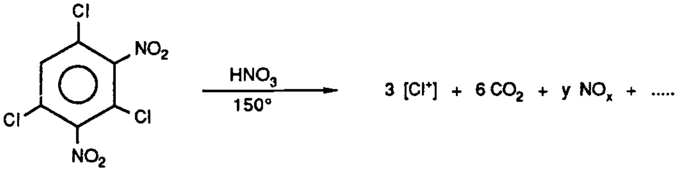
4 5

$$5 + 5\,NH_3 \xrightarrow[(H_2O)]{C_6H_5CH_3} 1 + 2\,NH_4Cl + CH_3OH$$

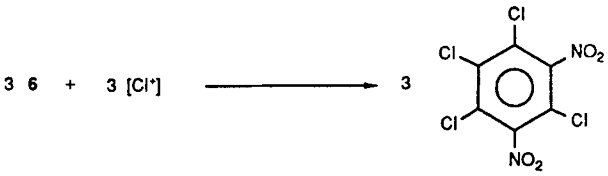
$$5 \xrightarrow[C_6H_5CH_3,\ 95°,\ 1\ hr]{SOCl_2,\ DMF} 3 + CH_3Cl + SO_2$$

DISCUSSION AND RESULTS

The conditions necessary to effect introduction of the third nitro group into the trichloro compound 2 to produce 3 were quite strenuous; excess 90 or 95% nitric acid (4.35 moles per mole of 2) and 25 or 20% oleum (20 moles) were used at a reaction temperature of 150°C with vigorous stirring for 2.5 hours.[1] After the reaction mixture was quenched with water, the product was isolated in 91% yield and 89% purity. The by-products were other nitrated chlorobenzenes, primarily 1,3,5-trichloro-2,4-dinitrobenzene (6) (3%) and 1,2,3,5-tetrachloro-4,6-dinitrobenzene (7) (8%). The conversion was 0.80 mole of 3 per mole of 2. For subsequent ammonolysis of 3 to 1 it was unnecessary to remove either 6 or 7, because both are quite unreactive toward ammonia. The tetrachloro compound 7 was formed from the dinitro intermediate 6 and chlorine (or a chlorinating species) that had been generated by oxidation of 6. For the optimum conditions of time, temperature, and concentrations studied, it was shown that a portion of the intermediate 6 (equivalent to approximately 0.03 mole per mole of the starting material 1) was oxidized to give carbon dioxide (0.18 mole) and the active chlo-



6



7

rine (0.09 mole), which then reacted with additional 6 (equivalent to 0.09 mole of 1) to give compound 7 (0.09 mole).

Because of the activating effect of a methoxyl group on electrophilic aromatic substitution, nitration of 4 would be expected to proceed more readily than nitration of 2. This was indeed found to be so, and 5 was obtained in excellent yield at lower temperature (100°C) without the necessity for a large excess of nitric acid or use of oleum, and without formation of a by-product analogous to 7. Owing to the rapidity of the reaction and the relatively mild conditions, development of a continuous process appears to be quite feasible. Complete conversions were obtained even when the excess of nitric acid was only five percent over the calculated amount; the reaction period was longer (two hours), and a higher temperature was used (125°C), but such a procedure is advantageous when use of minimum amount of nitric acid is desirable, such as for synthesis of the nitrogen-15 labeled analog.

Compound 5 has been prepared by a different route and for another purpose[5] starting with 2, which was nitrated to the dinitro compound 6. One of the chloro groups was displaced with sodium methoxide to give 3,5-dichloro 2,4-dinitroanisole, which was further nitrated to produce 5. The product was converted by basic hydrolysis to trinitrophloroglucinol.

Displacements of both the chloro and the methoxyl groups of 5 by ammonia occurred readily to give 1. Whether displacement of a methoxyl group was faster or slower than a chloro group was not determined, because the rates for introduction of the second and third amino groups were much faster than for the first. Consequently ammonolysis reactions using limited amounts of ammonia give a mixture of 1 and starting material (3 or 5), with only very small amounts of mono- and di-amino compounds. However, from reactions in which mixtures of 3 and 5 were treated with limited quantities of ammonia, it was found that 5 reacted several times faster than 3 (Table 1). Thus attack by ammonia probably occurred preferentially at the carbon bearing the methoxyl group, which is consistent with the electron deshielding evident from the ^{13}C-NMR chemical shift (146 ppm).

TABLE 1

Competitive Reactions of Dichlorotrinitroanisole (5) and Trinitrotrichlorobenzene (3) with Ammonia*

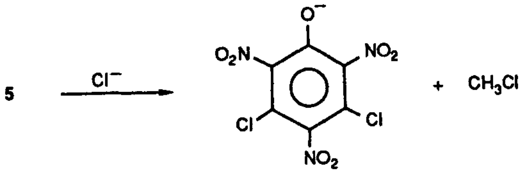
	Unreacted			Reacted		
NH_3	5	3	5/3	5	3	5/3
0.0	0.50	0.50	1.00	0.00	0.00	---
1.5	0.29	0.43	0.67	0.21	0.07	3.0
3.0	0.13	0.31	0.42	0.37	0.19	1.9
4.5	0.02	0.15	0.13	0.48	0.35	1.4
5.5	0.00	0.00	---	0.50	0.50	1.0

---

* Quantities are in millimoles. Limited quantities of ammonium hydroxide (15 M) were reacted with 5 and 3 (0.50 mmol each) in toluene (4 ml) for 2 days at room temperature. The filtered toluene solutions of unreacted 5 and 3 were evaporated, the residues were taken up in deuterochloroform, and the relative amounts of 5 and 3 were determined by quantitative ^{13}C-NMR spectroscopy.

For certain applications of 1 it is desirable that its median particle size be around 50 μm. To favor crystal growth of such an insoluble material to this size necessitated development of procedures in which the rate of ammonia introduction into a toluene reaction mixture containing 3 was controlled and the reaction temperature was 150°C.[1] Addition of water to the ammonolysis reaction reduces the small amount of ammonium chloride entrapped in the product crystals, but otherwise appears to have no affect on the reaction. Ammonolysis at low temperatures results in 1 precipitating as extremely small crystals. However, extensive side reactions occurred when ammonolysis of 5 was carried out at elevated temperatures. Various solvents and conditions were investigated, but pure product could be obtained only when the ammonolysis was conducted at temperatures below about 50°C. The material was thus of small particle size (90% of the particles were less than 10 μm), which for certain purposes is entirely satisfactory or perhaps preferable. Recrystallization of 1 is impractical on a large scale. When small amounts of material of extremely high purity are desired, however, 1 may be recrystallized with essentially complete recovery from dimethyl sulfoxide or diphenyl ether.

In the high temperature ammonolysis of 5 the principal side reaction is displacement of the methyl group by chloride ion to form the ammonium salt of 3,5-dichloro-2,4,6-trinitrophenol. The reaction does not occur at lower temperatures because of the insolubility of ammonium chloride in toluene. When better solvents for the chloride, such as dimethylformamide or dimethyl sulfoxide, are used or added to the toluene, the yield of 1 is greatly



8

reduced, even at low temperatures. Another side reaction that occurred in a closed system at elevated temperature was reduction of some of the nitro groups by the liberated methanol. When the ammonolysis reactions were conducted at ambient temperatures and in relatively non-polar solvents, none of these side reactions significantly affected the purity of 1, which was obtained in yields greater than 95%.

The dichloropicric acid, corresponding to 8, was readily converted to 3 with thionyl chloride and a catalytic amount of dimethylformamide. However, direct conversion of 5 to 3 can be accomplished in excellent yield and purity when a stoichiometric amount of dimethyl formamide is used. With catalytic amounts the reaction is slow, and (judging from the red color of the mixture) there was some reduction of nitro groups to azoxy. The first step in the displacement of methoxyl by chloro is probably elimination of the methyl group as methyl chloride followed by displacement of the oxygen function, either through the chlorosulfite ester or the Vilsmeier complex. Although producing 3 from 5 entails one additional step over its production from 2, the overall yield and conversion are higher, the product is of high purity (no by-product analogous to 7), conditions for the nitration of 4 are milder and offer the possibility for a continuous process, and less waste is generated.

EXPERIMENTAL PART

3,5-Dichloroanisole was purchased from the Aldrich Chemical Company. NMR spectra were obtained with a JEOL FX-90-Q spectrometer operating at 89.6 MHz for ^{1}H, 22.5 MHz for ^{13}C, 6.47 Mhz for ^{14}N, and 9.08 MHz for ^{15}N. Chemical-shift references

(∂ = 0 ppm) were tetramethylsilane for ^{1}H and ^{13}C and external nitromethane for ^{14}N and ^{15}N. Thin-layer chromatography (TLC) employed fluorescent silica gel plates (1 X 3 in., 200 µm layer thickness, MK6F, Whatman). Spots were visualized under ultraviolet light; exposure of the developed plates to ammonia vapor often produced spots that were visible and more intense under ultraviolet light. Melting points were determined on a Fisher-Johns Melting Point Apparatus.

3,5-Dichloro-2,4,6-trinitroanisole (5)

3,5-Dichloroanisole (35.4 g, 0.20 mol) was added over a period of 2 min to a stirred mixture of nitric acid (90%, 50 ml, 1.0 mol) and sulfuric acid (94%, 115 ml) in a 500-ml three-neck round-bottom flask cooled in an ice bath. The temperature of the mixture rose to 50°C. After 3 min the ice bath was removed, and the mixture was heated from 35°C to 100°C over a period of 8 min where it was held for 15 min. Samples for analysis by TLC (hexane/acetone, 9:1) were taken during the reaction period and showed the appearance and disappearance of the dinitro intermediate(s) (R_f 0.12) and, finally, the presence of only the product (R_f 0.42). The mixture was cooled to room temperature and poured onto ice. The product was filtered, washed with water, and dried (61.5 g, 98.6% yield); m.p. 94-95°C (95-95.5°C after recrystallization from toluene-hexane); ^{13}C-NMR ($CDCl_3$): ∂_{Me} = 64.6 ppm, ∂_1 = 146.0 ppm, $\partial_{3,5}$ = 122.2 ppm, $\partial_{2,6}$ = 143.0 ppm, ∂_4 = 143.7 ppm, $^{1}J_{C2-C3,\ C3-C4}$ = 82 Hz; ^{1}H-NMR ($CDCl_3$): ∂ = 4.11 ppm; $^{1}J_{C-H}$ = 149 Hz; ^{15}N-NMR ($CDCl_3$): $\partial_{2,6}$ = -24.9 ppm, ∂_4 = -24.8 ppm, $^{1}J_{C2,6-N}$ = 20.8 Hz, $^{1}J_{C4-N}$ = 19.5 Hz, $^{3}J_{C-N}$ = 2.5 Hz; DTA: melting endotherm 98°C, decomp. exotherm 275°C; impact sensitivity (Type 12/Type 12B): 124cm/131cm (crude), 112cm/119cm (recrystallized).

1,3,5-Trichloro-2,4,6-trinitrobenzene (3)

To a solution of 5 (0.624 g, 0.020 mol) in toluene (2 ml) at 50°C was added thionyl chloride (0.20 ml, 0.027 mol) and dimethylformamide (0.15 ml, 0.022 mol). The magnetically stirred mixture was heated to 95°C over a period of 15 min and maintained at that temperature for another hour. Periodic analysis during the reaction period by TLC (heptane/dioxane, 9:1) showed the disappearance of 5 (R_f 0.3) as it was converted to the product (R_f 0.4). The pale yellow solution was washed with water, dried over magnesium sulfate, treated with activated carbon, filtered, and evaporated to give a cream-colored solid (0.600 g. 95% yield); m.p. 194-195°C (195-196°C after recrystallization from acetic acid); ^{13}C-NMR ($CDCl_3$): $\partial_{1,3,5}$ = 122.4 ppm, $\partial_{2,4,6}$ = 147.5 ppm, $^{1}J_{C-C}$ = 81 Hz; ^{14}N-NMR ($CDCl_3$): ∂ = -26.0 ppm.

1,3,5-Triamino-2,4,6-trinitrobenzene (1)

A. A solution of 5 (3.12 g, 0.010 mol) in toluene (40 ml) in a 100-ml stainless-steel autoclave containing a Teflon-covered stirring bar was evacuated to the vapor pressure of toluene (30-40 mm Hg). Ammonia was admitted to the magnetically stirred autoclave from a 3.8-l cylinder. After 30 min the pressure had decreased from 19 psig to 14 psig (corresponding to 5.5 mmol of ammomia); the temperature of the vessel rose to about 30°C during the reaction. After the excess pressure was vented the autoclave was opened, the mixture was filtered, and the bright yellow product was washed sequentially with toluene, hot water, and acetone, and dried (2.47 g, 96% yield).

B. Ammonia was introduced over the surface of a vigorously stirred solution of 5 (2.56 g, 8.2 mmol) in toluene (40 ml) contained in a 100-ml round-bottom flask. After about 7 hr the supernatant solution over the pale yellow precipitate became colorless, and TLC analysis (toluene) showed the absence of starting material (R_f 0.88) and intermediates (R_f 0.47, 0.35). The ammonia flow was stopped, and the product was isolated as in A, above (1.99 g, 94% yield).

Analyses and properties of the products were typical for 1: ^{13}C-NMR (H_2SO_4): 155.7, 152.7, 151.5, 114.5, 114.3, 84.9 ppm; ^{1}H-NMR (H_2SO_4): 0.51 ppm relative to NH_4^+ = 0 ppm; ammonium chloride content <0.05%; DTA exotherm onset 340°C; particle size (% passing screens): 96% <45 µm, 94% <20 µm, 90% <10 µm; surface area: 1.82 m^2/g (Photelometer), 3.82 m^2/g (Quantasorb).

Recrystallization of TATB from either dimethyl sulfoxide (5 g/l at 145°C) or from diphenyl ether (2 g/l at 220°C) removed trace impurities with essentially complete recovery of the product.

ACKNOWLEDGEMENT

This work was performed under the auspices of the U. S. Department of Energy.

REFERENCES

1. T. M. Benziger, "Manufacture of Triaminotrinitrobenzene," Proceedings of the 1981 Annual Conference, Chemical & Mechanical Technologies of Propellants and Explosives, Fraunhofer Institut, Karlsruhe, German Federal Republic. T. M. Benziger, "Method for the Production of High-Purity Triaminotrinitrobenzene," U. S. Patent No. 4,032,377, June 1977.
2. H. H. Cady and A. C. Larson, Acta Crystallog. 18, 485 (1965).
3. C. L. Jackson and J. F. Wing, J. Am. Chem. Soc. 354 (1887).
4. R. L. Atkins, R. A. Hollins, and W. S. Wilson, J. Org. Chem., 51, 3261 (1986).
5. E. Ludolphy and A. Berthmann, "Process for Production of Trinitrophloroglucinol," German Patent 1543525, Sept. 1973; Chem. Abst. 80: 14763h.