

Improved Synthesis of TNT Isomers

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The syntheses of all of the isomers of TNT were studied in detail. Significant improvements to known procedures were found, thus making readily accessible highly pure samples of the TNT isomers.

In connection with investigations on 2,4,6-trinitrotoluene (α -TNT) purification, samples of 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, and 3,4,5-TNT were needed. Although 2,4,6- and 2,4,5-TNT can be purchased, we found that all of the isomers could be easily synthesized in our laboratories.

Syntheses of all of the TNT isomers have been reported: 2,4,6 (6); 2,4,5 (2, 5); 2,3,4 (2, 5); 2,3,5 (2); 2,3,6 (1, 2); and 3,4,5 (4, 7).

After encountering difficulties with the methods described in the literature, we found that peroxytrifluoroacetic acid in chloroform (or dichloromethane) rapidly oxidizes the dinitrotoluidines I, II, III, and IV in a single step to the corresponding TNT isomers (2,3,5-, 2,3,6-, 2,3,6-, and 3,4,5-) in excellent yield. Peroxytrifluoroacetic acid was described by Emmons (3). The 2,4,5- and 2,3,4-TNT isomers were prepared efficiently by nitration of the commercially available 3,4- and 2,3-dinitrotoluenes, followed by simple fractional recrystallization of the product mixtures.

Experimental

Gas chromatographic analysis. The compositions of reaction mixtures and the purity of the final products were determined by gas chromatography using flame ionization detection. The six TNT isomers can be separated by means of a 10-ft $\times$ $\frac{1}{8}$ -in. aluminum column packed with 25% Dow 550 on 100/120 mesh Chromasorb G. At a column temperature of 260°C and a flow rate of 20 ml/min He, the retention times for 2,4,6-, 2,3,6-, 2,3,5-, 2,4,5-, 2,3,4-, and 3,4,5-TNT were 9.6, 11.1, 12.3, 13.2, 15.3, and 17.6 min, respectively. The five TNT isomers, excluding 2,4,6-TNT, can also be separated on a 6-ft $\times$ $\frac{1}{8}$ -in. U-shaped glass column containing 5% SE-30 on 80/100 mesh Gas-Chrom Q. At a column temperature of 170°C, the retention times for 2,3,6-, 2,3,5-, 2,4,5-, 2,3,4-, and 3,4,5-TNT were 7.4, 8.8, 9.8, 11.0, and 13.7 min, respectively. This column would not resolve 2,4,6-TNT from the 2,3,6-isomer. The compositions of the mixtures described here were determined by measurement of peak areas without correction for detector response for the different isomers.

Synthesis of 2,3,4-TNT. A mixture of 10 grams of commercial 2,3-dinitrotoluene, 80 ml of 96% sulfuric acid, and 30 ml of 90% nitric acid in a 250-ml round-bottom flask was heated to 100–120°C, kept at that temperature for 15 min, allowed to cool, and poured over ice. The filtrate was collected, washed with water, and air dried. The proportions of isomers determined from gc peak areas were: 2,3,4-TNT (72%), 2,3,6-TNT (22%), and 2,3,5-TNT (6%). Recrystallization from methanol gave

3.8 grams of 2,3,4-TNT, mp 110–111°C, and pure gc. A second crop of 2,3,4-TNT was obtained, 0.6 gram, mp 109–111°C [lit., 112°C (1)]. Further fractional crystallization of the remaining residue yielded 0.4 gram of impure 2,3,6-TNT.

Synthesis of 2,3,5-TNT. Preparation of 2-methyl-4-nitroacetanilide. Two hundred grams of 2-methyl-4-nitroaniline (Aldrich) was suspended in 1600 ml of glacial acetic acid, the mixture cooled to 5°C, and 240 ml of acetic anhydride containing 0.5 gram of 96% sulfuric acid added dropwise (15 min). The temperature was raised to 85°C over 25 min during which time the desired product separated as a light brown solid. After the reaction temperature was held at 85°C for 10 min, the mixture was cooled to 40°C and poured into 4 liters of crushed ice. The light brown precipitate was filtered, washed with water, and dried under vacuum. Wt 248.6 grams; yield 97%.

Preparation of 2-methyl-4,6-dinitroacetanilide. A mixed acid solution was prepared by slowly adding 1034 ml of 96% sulfuric acid to 646 ml of 90% nitric acid, keeping the temperature of the mixture below 25°C. A 1680-ml sample of mixed acid was cooled to 5°C, and 240 grams of 2-methyl-4-nitroacetanilide added in small portions (45 min), maintaining the temperature at 4–7°C. After addition, the temperature was allowed to rise to 15°C, at which point the reaction was quenched on 6 liters of crushed ice. The cream-colored precipitate was filtered, washed thoroughly with water, and dried under vacuum. Wt 277.1 grams; yield 94%.

Preparation of 3,5-dinitro-2-aminotoluene. To a 206-gram sample of 2-methyl-4,6-dinitroacetanilide (0.87 mole) was added 1340 ml of 50% sulfuric acid with stirring. The mixture was heated on a steam bath at 80–90°C for 2 hr during which time a yellow-orange solid formed. The hot mixture was quenched on 8 liters of crushed ice and allowed to stand overnight. The solid was filtered, washed thoroughly with water to remove all traces of acid, and vacuum dried over sulfuric acid. Wt 159.6 grams; yield, 93%; mp 217–218°C.

Preparation of 2,3,5-TNT. Trifluoroacetic anhydride (570 ml) was added quickly (5 min) to 835 ml of CHCl_3 , keeping the temperature at about 5°C. A 90-ml sample of 90% hydrogen peroxide was added dropwise (2 hr), keeping the temperature between 0° and 5°C. To this milky white mixture was added 3,5-dinitro-2-aminotoluene (159.6 grams) in small portions (30 min) at 0–5°C. The reaction temperature was allowed to rise slowly to 54°C (40 min), the dropping funnel was replaced by a condenser, and the mixture was refluxed for 2 hr. The reaction was cooled to ambient temperature, and solvents were removed on a rotary evaporator until a yellow precipitate appeared. Methylene chloride was added to dissolve the precipitate, and the resulting solution washed with four 250-ml portions of 5% NaHCO_3 and two 250-ml portions of water. The methylene chloride solution was dried (MgSO_4), the solvent removed under vacuum, and the yellow-crystalline product dried under vacuum. The product (180.7 grams) represented a crude yield of 98%. Mp was 90–93°C, and purity was determined to be

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99% by gc analysis. Recrystallization from 1250 ml of methanol gave 124.3 grams of pure 2,3,5-TNT; mp 96–97°C [lit., 97°C (2)].

Synthesis of 2,3,6-TNT. Preparation of 2-methyl-3-nitroacetanilide. This intermediate was prepared from 2-methyl-3-nitroaniline (Aldrich) by a procedure similar to that described above for the preparation of 2-methyl-4-nitroacetanilide. Yield 92.5%.

Preparation of 2-methyl-3,4-dinitroacetanilide and 2-methyl-3,6-dinitroacetanilide. The nitration of 2-methyl-3-nitroacetanilide to a mixture of 2-methyl-3,4-dinitroacetanilide and 2-methyl-3,6-dinitroacetanilide was carried out by the same procedure described above for the synthesis of 2-methyl-4,6-dinitroacetanilide. Yield 94%.

Preparation of 3,4-dinitro-2-aminotoluene and 3,6-dinitro-2-amino-toluene. Hydrolysis of 2-methyl-3,4-dinitroacetanilide and 2-methyl-3,6-dinitroacetanilide was accomplished by the procedure described above in the preparation of 2,3,5-TNT. Yield 97.3%.

Preparation of 2,3,6-TNT. The oxidation of a mixture of 3,4-dinitro-2-aminotoluene and 3,6-dinitro-2-aminotoluene by the procedure described for the preparation of 2,3,5-TNT gave a 91.5% crude yield of 2,3,6-TNT, mp 105–112°C. Recrystallization from methanol gave a pale yellow solid, mp 111.5–112.5°C [lit., 111°C (3)], which was shown by gc analysis to be >99% pure.

Synthesis of 2,4,5-TNT. A mixture of 20 grams of 3,4-dinitrotoluene (Aldrich) in 160 ml of 96% sulfuric acid and 60 ml of 90% nitric acid was stirred and heated on a steam bath (30 min) at 80–90°C. The mixture was poured onto crushed ice, and the product was washed with water and collected by filtration. The product was air dried (25.1 grams), and analysis by gc showed 81% 2,4,5-TNT and 19% 2,3,4-TNT; no 3,4,5-TNT was detected. Recrystallization from 130 ml of boiling absolute ethanol gave 17.1 grams of nearly pure 2,4,5-isomer. A second recrystallization gave gas chromatographically pure 2,4,5-TNT in two crops, mp 104–104.5° [lit., 104°C (2)]. The yield of pure 2,4,5-TNT was 15.7 grams, 65%, based on the starting 3,4-dinitrotoluene.

Synthesis of 2,4,6-TNT. A 21.75-gram sample of 30.8% fuming sulfuric acid was cooled to 0°C, and 5.24 grams of 100% nitric acid added dropwise. This mixed acid solution was warmed to 24°C, and 5.05 grams of 2,4-TNT added in one portion. The temperature was then raised slowly (40 min) to 90°C and, after stirring an additional hour at 90°C, was quenched on 300-ml ice. Three 75-ml methylene chloride extracts were combined, dried (MgSO₄), and the solvent was removed under vacuum. The product, 6.00 grams, 95.2% yield, was greater than 99.9% 2,4,6-TNT by gc analysis.

Synthesis of 3,4,5-TNT. Preparation of 3,5-dinitro-4-aminotoluene. To a 3-liter sample of 90% nitric acid was

added a 300-gram sample of *N*-acetyl-*p*-toluidine (Aldrich) in small portions as quickly as possible, keeping the reaction temperature between 10° and 15°C by means of a Dry Ice-acetone bath. Rapid addition and low reaction temperature are essential to high yields. As soon as all the *N*-acetyl-*p*-toluidine dissolved, the reaction mixture was quenched on 3000 ml of crushed ice. The precipitate was filtered and was washed free of acid with water. The moist solid was heated for 1 hr at 80–90°C in 2 liters of 50% sulfuric acid. The resulting mixture was cooled to 20°C and filtered to give a yellow solid, which was washed and then dried under vacuum over H₂SO₄. Wt 284.1 grams; crude yield 72%; mp 167–169°C.

Preparation of 3,4,5-TNT. 3,5-Dinitro-4-aminotoluene was oxidized to 3,4,5-TNT by the procedure described above for the preparation of 2,3,5-TNT. Crude yield 94.4%; mp 126–132°C. One recrystallization from methanol gave essentially pure 3,4,5-TNT, mp 133–134°C [lit., 131–132°C (5) and 135°C (4)].

Discussion

The use of peroxytrifluoroacetic acid in oxidizing dinitrotoluidines to trinitrotoluenes is an important improvement over the use of Caro's acid as an oxidant. Although only three of the TNT isomers were prepared by the peroxytrifluoroacetic acid oxidation, the reaction appears to be general and applicable to many similar structures. A fourth, 2,4,5-TNT, can also be made in this manner by oxidation of 4,6-dinitro-3-aminotoluene, obtainable by the aminolysis of 4,6-dinitro-3-chlorotoluene; the latter is produced in high yield by nitration of the commercially available 3-chloro-4-nitrotoluene. However, the nitration of 3,4-dinitrotoluene to 2,4,5-TNT, which involves but one step, is the preferred method. The synthesis of 2,3,4-TNT through a peroxytrifluoroacetic acid oxidation is not attractive because of the great difficulty in preparing any of the three dinitrotoluidine isomers that might be used for this purpose.

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