3,4,5-Trinitrotoluene via Caro's Acid Oxidation

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An improved synthesis of 3,4,5-trinitrotoluene by the Caro's acid oxidation of 3,5-dinitro-4-aminotoluene is described.

THE previously published synthesis of 3,4,5-trinitrotoluene involves conversion of the 3,5-dinitro-4-aminotoluene to the diazonium salt and its subsequent reaction with sodium nitrite via a rather complicated procedure (*3*). We now report a simple two-step conversion of 3,5-dinitro-4-aminotoluene to 3,4,5-trinitrotoluene.

EXPERIMENTAL

3,4,5-Trinitrotoluene. Caro's acid was prepared by the method of Brady and Taylor (*1*) using 60 grams of finely powdered ammonium persulfate dissolved in 44 ml of cold concentrated sulfuric acid (*2*). The acid slurry and 100 grams of crushed ice were added to 9.95 grams (0.0198 mole) of 3,5-dinitro-4-aminotoluene [m.p. 171–2°; lit. (*1*) m.p. 171–71.5°] dissolved in 6 ml of concentrated sulfuric acid. A yellow precipitate formed immediately and the mixture was stirred for 48 hours. The 4-nitroso-3,5-dinitrotoluene, formed in nearly quantitative yield, was filtered, washed in water, dried, and used without further purification.

The 4-nitroso-3,5-dinitrotoluene was oxidized by adding it in small amounts to 100 ml of boiling concentrated nitric acid (sp. gr. 1.42). The mixture was boiled until all nitrogen oxide evolution ceased. Solid 3,4,5-trinitrotoluene precipitated upon addition of 200 ml of water. Washing with water, drying, and three recrystallizations (ethanol) produced 2.05 grams (18%) of greenish yellow prisms, [m.p. 131–32°; lit. (*3*) m.p. 135°; lit. (*4*) m.p. 137.5°].

The infrared spectrum (KBr pellet) was identical to that of a sample prepared by the method of Hodgson *et al.* (*3*), NMR (CD_3SOCD_3), $\delta = 3.02$ ppm (CH_3 singlet), and $\delta = 9.05$ ppm (ϕH singlet) (TMS internal standard).

3,4,5-Trinitrotoluene is a high explosive similar to 2,4,6-trinitrotoluene, which is a common ingredient of many military high explosives. It should therefore be handled with appropriate care.

LITERATURE CITED

(1) Brady, O.L., Taylor, L., *J. Chem. Soc.* **117**, 876 (1920).
(2) Fieser, L.F., Fieser, Mary, "Reagents for Organic Synthesis," p. 118, Wiley, New York, 1967.
(3) Hodgson, H.H., Mahedevan, A.P., Ward, E.E., *J. Chem. Soc.* **1947**, 1392.
(4) Körner, G., Contardi, A., *Atti Accad. Lincei* **24**, I, 888 (1915).

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CORRECTION

In the article "Solubility of Some Light Hydrocarbons and Hydrogen in Some Organic Solvents" by J. A. Waters, George A. Mortimer, and H. E. Clements [J. CHEM. ENG. DATA **15**, 174 (1970)], the heading of the third column of Table III on page 176 should read

Gas Solubility × 10^3,
Moles/Liter at 1 Atm.