Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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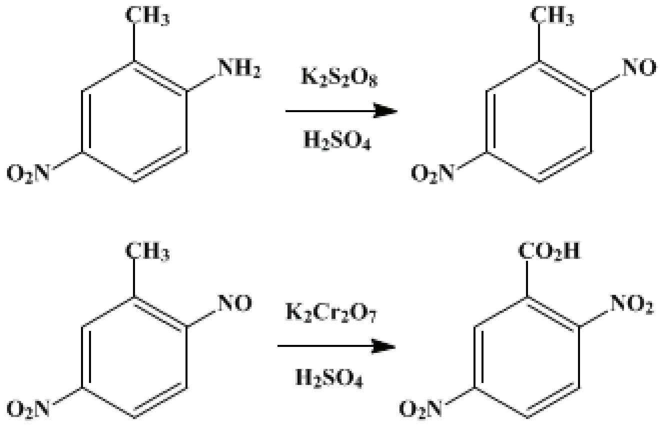
Organic Syntheses, Coll. Vol. 3, p.334 (1955); Vol. 22, p.44 (1942).

2,5-DINITROBENZOIC ACID

[Benzoic acid, 2,5-dinitro-]



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1. Procedure

A. 2-*Nitroso*-5-*nitrotoluene.* In a 5-l. round-bottomed flask fitted with a mechanical stirrer is placed 50 g. (0.33 mole) of pulverized 5-nitro-2-aminotoluene (Note 1). To this is added an ice-cold solution of 200 ml. of concentrated sulfuric acid in 50 ml. of water. While the suspension is stirred at room temperature, a solution of Caro's acid is prepared, as follows: to 175 ml. of ice-cold sulfuric acid (sp. gr. 1.84) in a 2-l. beaker is added 300 g. (1.11 moles) of pulverized potassium persulfate. The mixture is thoroughly stirred with a glass rod, and to it is added 900 g. of crushed ice and 300 ml. of water.

The well-stirred solution of Caro's acid is poured into the suspension of nitroaminotoluene. The mixture is stirred and warmed, but as soon as the temperature reaches 40°, heating is discontinued. After the solution has been stirred for 2 hours longer, an additional 100 g. (0.37 mole) of powdered potassium persulfate is added in one portion. The heat of reaction is sufficient to maintain the temperature at 40°. Stirring is continued for 2 hours more, and the suspension is then diluted with water to 4 l. The solid is filtered with suction (Note 2) and washed with 400 ml. of water. The wet material is transferred to a 5-l. round-bottomed flask, about 700 ml. of water is added, and the mixture is steam-distilled. The 2-nitroso-5-nitrotoluene is filtered from the distillate (Note 3). The total yield of air-dried product is 30–39 g. (55–71%) (Note 4).

B. 2,5-*Dinitrobenzoic acid*. A suspension of 20 g. (0.12 mole) of the air-dried 2-nitroso-5-nitrotoluene in 100 ml. of water is prepared in a 500-ml. Erlenmeyer flask, and to it is added 50 g. (0.17 mole) of powdered potassium dichromate (Note 5). The flask is placed in an ice-salt bath, and the mixture is stirred vigorously by means of an efficient stirrer. When the temperature has dropped to 5°, 175 ml. of concentrated sulfuric acid is added in a thin stream (Note 6) while the temperature is not allowed to exceed 35°. After all the sulfuric acid has been added the mixture is stirred and heated to 50°. The source of heat is removed, and the temperature is maintained between 50° and 55° by cooling in an ice bath as the exothermic reaction takes place (Note 7). After 20 minutes the temperature is raised to 65° ± 3° and held there for 1 hour longer.

The solution is cooled to 20°, and 250 g. of ice is added. The mixture is stirred for a few minutes, then is filtered with suction (hardened filter paper), and the solid is washed with 35 ml. of ice water. The solid is suspended in 25 ml. of water in a 600-ml. beaker and is slowly dissolved by gradual addition of 55–65 ml. of a 10% solution of sodium carbonate. The solution is filtered (Note 8), and the filtrate is made strongly acidic to Congo red by addition of 1:1 hydrochloric acid. The mixture is chilled in ice for an hour and is then filtered. The product is washed with 12 ml. of ice water and air-dried. The acid melts at 174–176° and weighs 14–17 g. (55–66%). The acid may be recrystallized by dissolving 10 g. of it in 250 ml. of boiling 5% hydrochloric acid (Note 9). The solution, when chilled in ice, deposits 9.4 g. of 2,5-dinitrobenzoic acid as nearly colorless crystals which melt at 177–178° (Note 10).

2. Notes

1. Eastman Kodak Company's practical grade was used.
2. The filtrates, on standing overnight, deposit 5–5.6 g. of crude 2-nitroso-5-nitrotoluene, which is not included in the weights recorded. It may be added to the product obtained by steam distillation.
3. The submitters reported that successive 2.5-l. portions of distillate were filtered, and the following weights of product were obtained: 14.5, 10.7, 9.0, and 2 g., or 36.2 g. in 10 l. From one run the checkers obtained 19, 12, 6, and 2 g., or 39 g. In some runs it was necessary to collect 15–30 l. of distillate in order to obtain a 30-g. yield. The submitters report that unchanged amine, if present during the steam distillation, condenses with the nitroso compound, giving tarry products, and the yield of nitroso compound is reduced.
4. In favorable cases, the product is white and melts at 135–136°.
5. The procedures given in *Org. Syntheses* Coll. Vol. **1**, 385, 528 (1932), 392, 543 (1941), are not suitable for the oxidation of nitrosonitrotoluenes. Using the procedure given on p. 385 (1932) and p. 392 (1941) the yield of dinitro acid is low, and using the procedure given on p. 528 (1932) and p. 543 (1941) the dinitro acid is deeply colored.
6. This requires 20–25 minutes.
7. In a run twice this size the checkers observed that at this stage some of the semi-solid material on the top of the stirred solution burned. The burning ceased after a few minutes. The yield of final product was slightly lower. It must be emphasized that careful control of the temperature is necessary during the oxidation with dichromate in order to prevent the reaction from becoming too vigorous.
8. The undissolved residue is largely 2,5-dinitrotoluene, which may be used in subsequent oxidations. Larger yields of this compound may be obtained by shortening the time of stirring during the oxidation process.
9. Additional data on the recrystallization of 2,5-dinitrobenzoic acid are: a solution of 6.83 g. in 200 ml. of boiling toluene, when filtered and chilled, furnished 5.9 g.; a solution of 10 g. in 110 ml. of boiling water, when filtered and chilled, furnished 9.18 g.
10. When 3-nitro-4-aminotoluene was used, 3,4-dinitrobenzoic acid was obtained in approximately the same yields as those recorded for 2,5-dinitrobenzoic acid. The submitter reports: "3-nitro-4-aminotoluene dissolves readily in the sulfuric acid when the Caro's acid is added, and the 3-nitro-4-nitrosotoluene which separates is practically free of the amine. Therefore, the steam distillation may be omitted and the nitroso compound may be oxidized directly to the dinitro acid, which is obtained as a light-colored product. From 100 g. of 3-nitro-4-aminotoluene there was obtained 102 g. of yellow nitrosonitrotoluene which, when oxidized, gave 85 g. of 3,4-dinitrobenzoic acid melting at 158–162°. One crystallization gave the pure acid. A solution of 10 g. of the acid in 210 ml. of boiling water gave, after cooling, 9.1 g. of the acid. Similarly, a solution of 10 g. of the acid in 280 ml. of hot 5% hydrochloric acid was filtered quickly and then cooled. The filtrate deposited 9.4 g. of the acid."

3. Discussion

2,5-Dinitrobenzoic acid has been prepared by nitration of *o*-nitrobenzoic acid and fractional crystallization of the acids as the barium salts;[1] and by oxidation of 2,5-dinitrotoluene.[2]

References and Notes

1. Griess, *Ber.*, **7**, 1223 (1874).
2. Grell, *Ber.*, **28**, 2564 (1895).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

Caro's acid

nitrosonitrotoluenes

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

dichromate

sodium carbonate (497-19-8)

toluene (108-88-3)

barium (7440-39-3)

potassium dichromate (7778-50-9)

potassium persulfate (7727-21-1)

o-nitrobenzoic acid (552-16-9)

3-nitro-4-aminotoluene (89-62-3)

5-nitro-2-aminotoluene (99-52-5)

2,5-Dinitrobenzoic acid,
Benzoic acid, 2,5-dinitro- (610-28-6)

nitroaminotoluene

2-Nitroso-5-nitrotoluene (57610-10-3)

2,5-dinitrotoluene (619-15-8)

3,4-dinitrobenzoic acid (528-45-0)

3-nitro-4-nitrosotoluene

nitrosonitrotoluene