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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 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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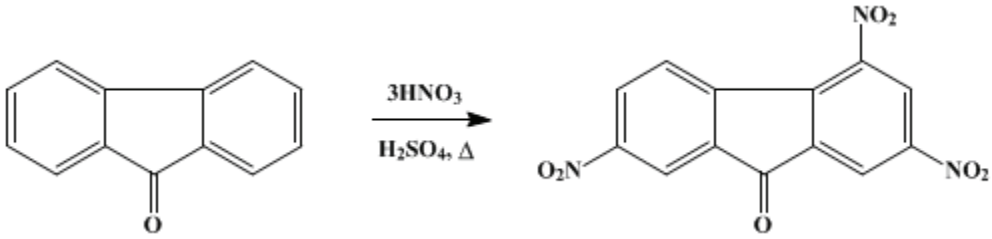
2,4,7-TRINITROFLUORENONE

[9-Fluorenone, 2,4,7-trinitro-]



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1. Procedure

In a well-ventilated hood, a 250-ml. dropping funnel, a thermometer, and a mechanical stirrer are connected by ground-glass joints to a 3-l. three-necked round-bottomed flask. Nine hundred milliliters of red fuming nitric acid (sp. gr. 1.59–1.60) is placed in the flask, and 675 ml. of concentrated sulfuric acid (sp. gr. 1.84) is added with stirring. The acid mixture is cooled to 20°, and the cooling bath is removed. A solution of 45 g. (0.25 mole) of fluorenone (Note 1). in 135 ml. of glacial acetic acid is added dropwise to the mixed acids over a period of about 40 minutes (Note 2). At the end of the addition, the temperature of the reaction mixture is about 45°. The stirrer, thermometer, and funnel are removed, the flask is attached to a reflux condenser with a ground-glass joint, and ground-glass stoppers are placed in the other two openings. The reaction mixture is refluxed for 1 hour and then poured (in the hood) slowly with shaking onto 7 kg. of cracked ice in a 12-l. flask. The product separates as a yellow solid and is filtered by suction and washed with 5 l. of water. The product and 2 l. of water are placed in a 5-l. round-bottomed flask, and steam is passed into the mixture for 1 hour to dissolve and remove acidic impurities (Note 3). The product is filtered by suction, washed with water until the washings are no longer acid to Congo red paper, and air-dried overnight. The material is further dried in a 1-l. round-bottomed flask connected to a water pump and heated in a water bath at 80–90° for several hours. The product is a yellow powder weighing 72–74 g. (91–94%) and melting at 166–171° (Note 4).

The crude product is dissolved in 350 ml. of boiling glacial acetic acid, and the hot solution is filtered by suction (Note 5). Any crystals that separate during the filtration are redissolved by heating the suction flask, and the solution is allowed to cool slowly. The small yellow needles that separate are filtered with suction and washed successively with small quantities of ethanol (30 ml.), water (50 ml.), and ethanol (30 ml.). The yield is 59–61 g. (75–78%) of 2,4,7-trinitrofluorenone, melting at 175.2–176.0°. Additional material can be recovered from the mother liquor by dilution with water, drying the precipitate so formed, and recrystallization from acetic acid. The second crop consists of about 5 g. of pure material, melting at 175.2–176.0°, which usually has a slightly darker color than the first crop.

2. Notes

1. Commercial fluorenone was recrystallized from benzene-ethanol to give material melting at 83–84°. Fluorenone can also be prepared conveniently from commercial fluorene according to the procedure of Huntress, Hershberg, and Cliff.[1] When the checkers nitrated unrecrystallized commercial fluorenone, m.p. 79–82°, the product obtained (yield 55.5 g.) was of a duller yellow color but melted at 175.5–176.5°.
2. Nitrogen oxides are evolved vigorously if the acetic acid solution of fluorenone is added to the acid mixture too rapidly.
3. If this treatment is omitted the recrystallized product has a brown color which is not removed by repeated recrystallizations.
4. The checkers observed melting points of 165–169° for the crude product.

5. Filter paper is not satisfactory for the filtration of hot acetic acid; a sintered-glass Büchner funnel is recommended.

3. Discussion

2,4,7-Trinitrofluorenone has been prepared by the nitration of fluorenone,[2,3] 2,7-dinitrofluorenone,[4] and 2,5-dinitrofluorenone.[4] The present method has been published[5] in connection with reports of the use of the reagent for the conversion of aromatic compounds to solid derivatives.

References and Notes

1. Huntress, Hershberg, and Cliff, *J. Am. Chem. Soc.*, **53**, 2720 (1931).
2. Schmidt and Bauer, *Ber.*, **38**, 3760 (1905). The material reported by these authors as 2,6,7-trinitrofluorenone was subsequently shown to be the 2,4,7-isomer (Bell, *J. Chem. Soc.*, **1928**, 1990).
3. Schmidt, Retzlaff, and Haid, *Ann.*, **390**, 231 (1912).
4. Ray and Francis, *J. Org. Chem.*, **8**, 58 (1943).
5. Orchin, Reggel, and Woolfolk, *J. Am. Chem. Soc.*, **69**, 1225 (1947); Orchin and Woolfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946).

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

nitrogen oxides

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

nitric acid (7697-37-2)

benzene-ethanol (60-12-8)

fluorene (86-73-7)

2,4,7-Trinitrofluorenone,
9-Fluorenone, 2,4,7-trinitro- (129-79-3)

fluorenone (486-25-9)

2,7-dinitrofluorenone (31551-45-8)

2,5-dinitrofluorenone

2,6,7-trinitrofluorenone