



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.

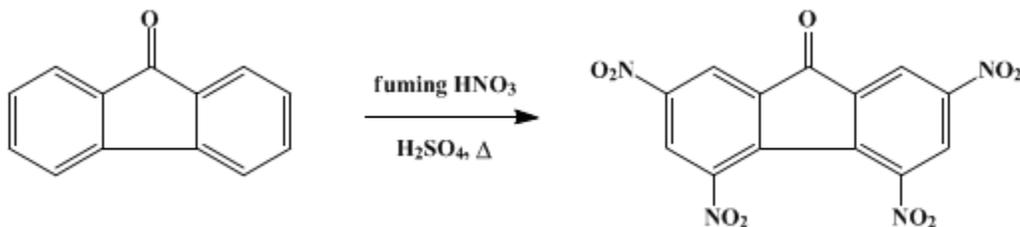
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.1029 (1973); Vol. 42, p.95 (1962).

2,4,5,7-TETRANITROFLUORENONE

[9-Fluorenone, 2,4,5,7-tetranitro-]



Submitted by Melvin S. Newman and H. Boden¹.

Checked by William E. Parham, Peter Delvigs, and E. Leete.

1. Procedure

A 5-l. three-necked flask fitted with an all-glass addition funnel and two condensers is charged with 770 ml. of concentrated **sulfuric acid** and 1.3 l. of 90% fuming **nitric acid** (Note 1). The solution is heated under gentle reflux, and a solution of 73 g. (0.4 mole) of **9-fluorenone** (Note 2) in 840 ml. of concentrated **sulfuric acid** (Note 3) is added from the dropping funnel over a 1-hour period. After the **fluorenone** addition is complete, a solution of 950 ml. of fuming **nitric acid** in 1120 ml. of concentrated **sulfuric acid** is added dropwise during 8.5 hours to the gently refluxing reaction mixture. The heating jacket is turned off and the solution is allowed to stand for 10 hours. The reaction mixture is poured into 5 gallons of water in two 5-gal. crocks (Note 4). The light yellow precipitate is washed with water, twice by decantation, filtered, washed several times with water and sucked dry, and finally is dried in a vacuum oven at 80° for 10 hours (Note 5). The yield of crude **2,4,5,7-tetranitrofluorenone**, m.p. 249–253°, is 105–117 g. (72–80%). This solid is recrystallized from 1.6 l. of **acetic acid** containing 100 ml. of **acetic anhydride**. The hot solution is filtered through a fluted filter and cooled rapidly to yield 80–86 g. (51–54%) of **2,4,5,7-tetranitrofluorenone**, m.p. 253.0–254.5° cor. (Note 6) and (Note 7).

2. Notes

1. Baker Analyzed reagent grade fuming **nitric acid** may be added to the **sulfuric acid** without special precautions, since the heat effect is not large.
2. Eastman white label **9-fluorenone**, m.p. 82–84°, was used. The checkers used material, m.p. 83.5–84.5°, prepared from **fluorene**.²
3. The deep purple-brown solution may have to be warmed in order to dissolve all the **fluorenone**.
4. This operation must be carried out in the hood.
5. The product may be dried under reduced pressure over **calcium chloride** for several days.
6. Additional product amounting to 15–17% may be obtained by recrystallization of further crops from the mother liquor.
7. **Tetranitrofluorenone** crystallizes with 0.5 mole of **acetic acid** which is readily lost on heating under reduced pressure.

3. Discussion

The procedure described here is essentially that of Newman and Lutz.³ **2,4,5,7-Tetranitrofluorenone** has been prepared by nitration of **fluorenone**,⁴ **2,4,7-trinitrofluorenone**,^{5,6} and **4,5-dinitrofluorenone**.⁶ The preparation by Schmidt et al.,^{4,5} which supposedly yielded the 2,3,6,7-isomer, has been shown⁶ to yield the 2,4,5,7-isomer.

4. Merits of Preparation

The complexes which **2,4,5,7-tetranitrofluorenone** forms with aromatic compounds are in general

higher melting and less soluble than are the corresponding complexes of 2,4,7-trinitrofluorenone.^{3,7}

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 1031](#)

References and Notes

1. Department of Chemistry, Ohio State University, Columbus, Ohio.
 2. E. B. Hershberg and I. S. Cliff, *J. Am. Chem. Soc.*, **53**, 2720 (1931).
 3. M. S. Newman and W. B. Lutz, *J. Am. Chem. Soc.*, **78**, 2469 (1956).
 4. J. Schmidt, F. Retzlaff and A. Haid, *Ann.*, **390**, 210 (1912).
 5. J. Schmidt and K. Bauer, *Ber.*, **38**, 3758 (1905).
 6. F. E. Ray and W. C. Francis, *J. Org. Chem.*, **8**, 52 (1943).
 7. M. Orchin, L. Reggel, and E. O. Woolfolk, *J. Am. Chem. Soc.*, **69**, 1225 (1947).
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Appendix

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

[calcium chloride \(10043-52-4\)](#)

[sulfuric acid \(7664-93-9\)](#)

[acetic acid \(64-19-7\)](#)

[acetic anhydride \(108-24-7\)](#)

[nitric acid \(7697-37-2\)](#)

[fluorene \(86-73-7\)](#)

[2,4,7-Trinitrofluorenone \(129-79-3\)](#)

[fluorenone,
9-fluorenone \(486-25-9\)](#)

[2,4,5,7-Tetranitrofluorenone,
9-Fluorenone, 2,4,5,7-tetranitro- \(746-53-2\)](#)

[Tetranitrofluorenone](#)

[4,5-dinitrofluorenone](#)