



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.

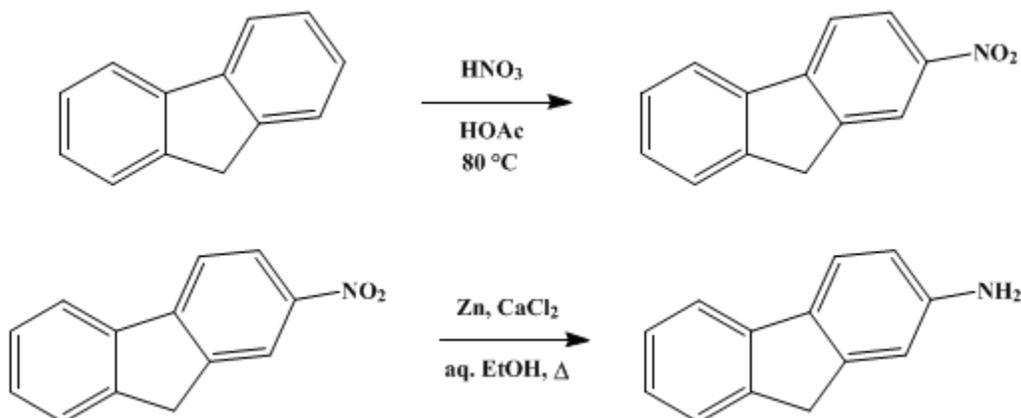
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.447 (1943); Vol. 13, p.74 (1933).

2-NITROFLUORENE AND 2-AMINOFLUORENE

[Fluorene, 2-nitro-, and 2-Fluorenylamine]



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1. Procedure

(A) *2-Nitrofluorene*.—Sixty grams (0.36 mole) of fluorene (Note 1) is dissolved in 500 cc. of warm glacial acetic acid in a 1-l. three-necked flask fitted with a thermometer, a mechanical stirrer, and a dropping funnel, and supported in a water bath. The temperature is brought to 50° , and 80 cc. (1.3 moles) of concentrated nitric acid (sp. gr. 1.42) is added with stirring in the course of fifteen minutes. During the addition, the solution becomes slightly yellow, and a small amount of material precipitates. The water bath is slowly brought to $60\text{--}65^\circ$, when the precipitate dissolves and the color of the solution deepens. Stirring is continued, and heat is applied continuously until the temperature of the mixture reaches 80° (Note 2). After five minutes, the water bath is removed, and the mixture, which now consists of a semi-solid paste of fine, yellow needles, is allowed to cool to room temperature during two hours. The product is collected on a Büchner funnel, sucked as dry as possible, and washed with two 25-cc. portions of cold glacial acetic acid containing 0.5 g. of potassium acetate. It is then washed several times with water and dried. The 2-nitrofluorene so obtained melts at $155\text{--}156^\circ$ and is sufficiently pure for most purposes. The yield is 60 g. (79 per cent of the theoretical amount).

If a purer product is desired, the above material may be crystallized from 200 cc. of glacial acetic acid. The purified product melts at 157° and weighs 56 g.

(B) *2-Aminofluorene*.—In a 2-l. round-bottomed flask, 30 g. (0.14 mole) of dried and powdered 2-nitrofluorene is made into a thin paste with 1 l. of 78 per cent alcohol (820 cc. of 95 per cent alcohol and 180 cc. of water). A solution of 10 g. of calcium chloride in 15 cc. of water, together with 300 g. of zinc dust, is added to the suspension, and the whole is thoroughly mixed. The flask is fitted with an effective reflux condenser, and the mixture is refluxed for two hours.

The sludge of zinc dust and zinc oxide is filtered from the boiling solution and extracted (Note 3) with 50 cc. of boiling 78 per cent alcohol. The combined filtrates are then poured into 2 l. of water, whereupon a white, flocculent precipitate is obtained. This is filtered with suction and recrystallized from 400 cc. of hot 50 per cent alcohol. The purified 2-aminofluorene crystallizes in needles melting at 127.5° . The yield is 20–21 g. (78–82 per cent of the theoretical amount).

2. Notes

1. The fluorene used had a melting point of $113\text{--}114^\circ$ and was obtained from the Gesellschaft für

Teerverwertung, Duisberg-Meiderich.

2. The reaction is exothermic at this point, and the temperature of the reaction mixture may be expected to rise ten to fifteen degrees above that of the surrounding bath. If the temperature is allowed to rise above 85°, the [2-nitrofluorene](#) will be highly colored and impure.

3. The sludge of [zinc](#) dust and [zinc oxide](#) is filtered while hot, through a previously warmed filter. Unless the solution is kept near the boiling point, some of the compound will crystallize during the filtration. If a small amount of [zinc](#) dust runs through the filter paper, it is advisable to heat the filtrate to the boiling point and refilter without suction through a folded filter paper in a hot water or steam jacket.

3. Discussion

The procedures given are essentially those of Diels.¹ [2-Nitrofluorene](#) has also been prepared by passing nitrous vapors into a [benzene](#) solution of [fluorene](#).²

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 30](#)

References and Notes

1. Diels, Ber. **34**, 1758 (1901).
2. Monti, Martello, and Valente, Gazz. chim. ital. **66**, 31 (1936).

Appendix

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

[alcohol](#) (64-17-5)

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

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

[Benzene](#) (71-43-2)

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

[zinc](#) (7440-66-6)

[zinc oxide](#)

[potassium acetate](#) (127-08-2)

[2-Nitrofluorene,](#)
[Fluorene, 2-nitro-](#) (607-57-8)

[2-Aminofluorene,](#)
[2-Fluorenylamine](#) (153-78-6)

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

