



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](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.

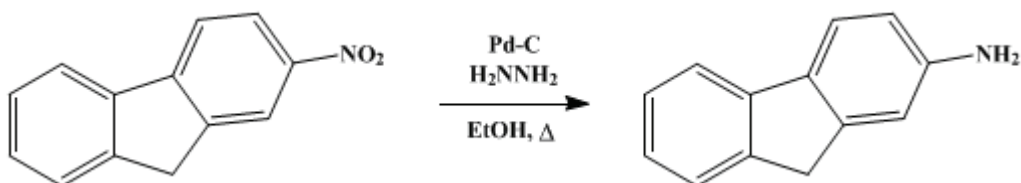
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.30 (1973); Vol. 40, p.5 (1960).*

## 2-AMINOFLUORENE

### [2-Fluorenylamine]



Submitted by P. M. G. Bavin<sup>1</sup>

Checked by John C. Sheehan and Roger E. Chandler..

### 1. Procedure

In a 2-l. three-necked round-bottomed flask, equipped with a mechanical stirrer (Note 1), reflux condenser, and dropping funnel, are placed 30 g. of pure 2-nitrofluorene, m.p. 157° [*Org. Syntheses, Coll. Vol. 2, 447 (1943)*], and 250 ml. of 95% ethanol. After warming to 50° on a steam bath, 0.1 g. of palladized charcoal catalyst (previously moistened with alcohol) is added (Note 2) and the stirrer is started. About 15 ml. of hydrazine hydrate is added from the dropping funnel during 30 minutes (Note 3). At this point an additional 0.1 g. of catalyst (previously moistened with alcohol) is added and the mixture is heated until the alcohol refluxes gently. After 1 hour the nitrofluorene has dissolved completely and the supernatant liquor is almost colorless.

The catalyst is removed by filtration with gentle suction through a thin layer of Celite (Note 4). The flask is rinsed with 30 ml. of hot alcohol which is then used to wash the catalyst and Celite. The combined filtrates are concentrated under reduced pressure to about 50 ml. (Note 5) and then heated to boiling at atmospheric pressure. When 250 ml. of hot water is added slowly, 2-aminofluorene is precipitated as a colorless, crystalline powder. After cooling in an ice bath, the 2-aminofluorene is collected, washed with water, and dried in the dark in a vacuum desiccator. The product melts at 127.8–128.8° (Note 6) and amounts to 24–25 g. (93–96%).

### 2. Notes

1. If the stirring is omitted, the nitrofluorene takes longer to dissolve.
2. A suitable catalyst is 10% palladium-on-charcoal, such as is supplied by Baker and Company, Inc., 113 Astor Street, Newark 5, New Jersey.
3. The reaction is exothermic, and too rapid addition of the hydrazine may cause the mixture to foam out of the condenser.
4. *Caution! The catalyst is often pyrophoric and should be kept moistened with alcohol.* Celite is a diatomaceous earth filter aid.
5. A rotary evaporator is very convenient for the concentration since some of the amine invariably crystallizes toward the end.
6. The melting point is that reported in *Organic Syntheses, Coll. Vol. 2, 448 (1943)*, for a recrystallized sample.

### 3. Discussion

The preparation of 2-aminofluorene reported previously in *Organic Syntheses* [Coll. Vol. 2, 448 (1943)] we based on the method of Diels.<sup>2</sup>

The present procedure illustrates a general method for the reduction of aromatic nitro compounds to aromatic amines using hydrazine and a hydrogenation catalyst such as palladium, platinum, nickel, iron, or rethenium. The literature on this procedure up to 1963 has been reviewed.<sup>3</sup> In many instances the catalytic hydrazine reductions give yields of amine equal to or better than those obtained by direct

catalytic hydrogenation or other reduction methods. Both the apparatus and the procedure are simple. Under appropriate conditions the method may be used for the dehalogenation of aliphatic and aromatic halides,<sup>3</sup> a reaction for which [palladium](#) appears to be a specific catalyst. The method has also been used for the reduction of [azobenzene](#) and [azoxybenzene](#) to [hydrazobenzene](#) (80–90%),<sup>4</sup> as well as for the synthesis of steroid aziridines by reduction of mesylate esters by vicinal azido alcohols (using [Raney nickel](#)).<sup>5</sup>

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## References and Notes

1. National Research Council of Canada Post-doctorate Fellow, 1954-56, at the University of Ottawa, Ottawa, Ontario.
  2. O. Diels, *Ber.*, **34**, 1758 (1901).
  3. A. Furst, R. C. Berlo, and S. Hooton, *Chem. Rev.*, **65**, 51 (1965).
  4. P. M. G. Bavin, *Can. J. Chem.*, **36**, 238 (1958).
  5. K. Ponsold, *Ber.*, **97**, 3524 (1964).
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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

2-Fluorenylamine

palladized charcoal catalyst

palladium-on-charcoal

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

[iron](#) (7439-89-6)

[platinum](#) (7440-06-4)

[nickel](#),  
[Raney nickel](#) (7440-02-0)

[palladium](#) (7440-05-3)

[hydrazine hydrate](#) (7803-57-8)

[hydrazine](#) (302-01-2)

[Azoxybenzene](#) (495-48-7)

[Azobenzene](#) (103-33-3)

[2-Nitrofluorene](#) (607-57-8)

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

Nitrofluorene

rethenium

hydrazobenzene (122-66-7)

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