



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.

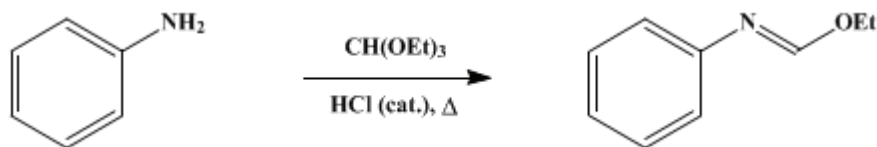
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 4, p.464 (1963); Vol. 35, p.65 (1955).*

## ETHYL N-PHENYLFORMIMIDATE

[Formimidic acid, N-phenyl-, ethyl ester]



Submitted by Royston M. Roberts and Paul J. Vogt<sup>1</sup>.

Checked by T. L. Cairns and J. J. Drysdale.

### 1. Procedure

A 500-ml. flask is equipped with a capillary through a side opening, and 94 g. (1.01 moles) of *aniline* and 1 ml. of concentrated *hydrochloric acid* are added. A 12-in. glass-helix-packed column is attached (Note 1), and the water introduced with the acid is removed by boiling; about 1 ml. of *aniline* is collected after the water has distilled. The flask and its contents are then cooled to room temperature, and 222 g. (1.50 moles) of *ethyl orthoformate* is added. The column is reattached, and *ethanol* (Note 2) is distilled as it is produced; the theoretical amount (92 g., 116 ml.) is obtained in about 2.25 hours.

The reaction mixture is allowed to cool slightly, and the pressure is lowered to 40 mm. (Note 3). The excess *ethyl orthoformate* is distilled at 65°/40 mm. After a small intermediate fraction of about 4 g., b.p. 65–117°/40mm., the product distils at 117–118°/40mm. (b.p. 87–88°/10mm.;  $n_D^{25}$  1.5248); the yield is 118–127 g. (78–84%). The residue amounts to about 14 g. and is mainly *N,N'*-diphenylformamidine (Note 4).

### 2. Notes

1. A Vigreux column may also be used since it is not difficult to separate the *ethanol* from *ethyl orthoformate*, the next most volatile component present. A total reflux, partial take-off head was used. Heat was supplied by an electric mantle; the column was heated with a glass-covered heating tape during the distillation of excess *ethyl orthoformate* and product.
2. A small amount (5–10 ml.) of lower-boiling material usually comes over before the *ethanol*; this is probably *ethyl formate*, produced by hydrolysis of the *ethyl orthoformate*.
3. A pressure regulator may conveniently be used in conjunction with a water aspirator.
4. If several runs are to be made, the residue may be saved and used as starting material, since the reaction proceeds via the initial formation of *N,N'*-diphenylformamidine and its subsequent reaction with *ethyl orthoformate*.<sup>2,3</sup>

### 3. Discussion

*Ethyl N-phenylformimidate* has been prepared from *silver formanilide* and *ethyl iodide*,<sup>4</sup> and from *aniline* and *ethyl orthoformate*.<sup>3</sup> This method incorporates the discovery<sup>2</sup> of the necessity of acid catalysis for satisfactory yields by the latter process.

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### References and Notes

1. University of Texas, Austin, Texas.
2. Roberts, *J. Am. Chem. Soc.*, **71**, 3848 (1949).
3. Claisen, *Ann.*, **287**, 363 (1895); Roberts and Vogt, *J. Am. Chem. Soc.*, **78**, 4778 (1956).
4. Comstock and Clapp, *Am. Chem. J.*, **13**, 527 (1891).

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

aniline (62-53-3)

Ethyl orthoformate

ethyl formate (109-94-4)

N,N'-diphenylformamidine

Ethyl iodide (75-03-6)

Ethyl N-phenylformimidate,  
Formimidic acid, N-phenyl-, ethyl ester (6780-49-0)

silver formanilide