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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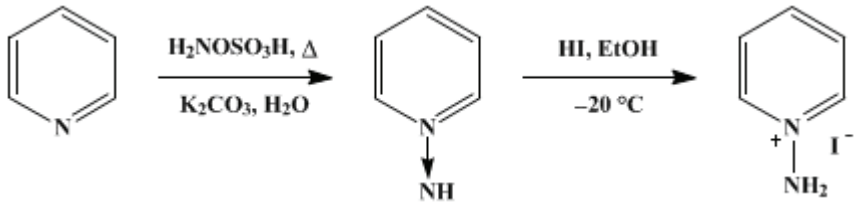
# 1-AMINOPYRIDINIUM IODIDE

## [Pyridinium, 1-amino-, iodide]

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## 1. Procedure

To a freshly prepared solution of 11.3 g. (0.10 mole) of hydroxylamine-O-sulfonic acid (Note 1) in 64 ml. of cold water there is added 24 ml. (24 g., 0.30 mole) of pyridine (Note 2). The mixture is heated at about 90° on a steam bath for 20 minutes. It is then cooled to room temperature with stirring, and 13.8 g. (0.10 mole) of potassium carbonate is added. The water and excess pyridine are removed from the mixture by heating it at 30–40° in a rotatory evaporator in conjunction with a water aspirator. The residue is treated with 120 ml. of ethanol, and the insoluble precipitate of potassium sulfate is removed by filtration.

Fourteen milliliters (22 g., 0.10 mole) of 57% hydriodic acid is added to the filtrate, and the resulting solution is stored at −20° for 1 hour (Note 3). The solid that separates is collected; weight 15.5–17.5 g. Recrystallization of this solid from about 100 ml. of absolute ethanol gives 14–16 g. (63–72%) of 1-aminopyridinium iodide as almost-white crystals, m.p. 160–162° (Note 4).

## 2. Notes

1. Hydroxylamine-O-sulfonic acid may be purchased from Ventron Corporation or prepared according to the directions in *Inorganic Syntheses*.[2]
Because aqueous solutions of hydroxylamine-O-sulfonic acid are not very stable, it is very important to use freshly prepared solutions. The purity of hydroxylamine-O-sulfonic acid should be checked by iodometric titration. If it is less than 85–90% pure, the yield of 1-aminopyridinium iodide will suffer. The acid can be purified by dissolving it in an equal weight of water and then precipitating it by stirring 7 volumes of acetic acid into the solution.
2. The pyridine was distilled before use. When the conversion is carried out in the presence of potassium carbonate using an equimolar amount of pyridine instead of an excess, the yields obtained are 20–30% lower.[3]
3. The temperature is kept at −20° or lower by a bath of dry ice and methanol. If the temperature rises above −20°, an appreciable quantity of 1-aminopyridinium iodide may redissolve and be lost.
4. The melting point recorded for 1-aminopyridinium iodide is 161–162°.[3]

## 3. Discussion

The formation of 1-aminopyridinium chloride has been accomplished by the acid hydrolysis of N-(*p*-acetaminobenzenesulfonimido) pyridine.[4] Also, the rearrangement of a substituted diazepine has been observed to give a 1-aminopyridine derivative.[5] The present procedure is an adaptation of that described by Gösl and Meuwsen.[3]

## 4. Merits of the Preparation

This procedure is a convenient and general method for preparing asymmetrically substituted

hydrazines.[3] This is illustrated by the following examples reported by the submitters[3] (% yields in parentheses): methylamine to methylhydrazinium hydrogen sulfate (49–53%); ethylamine to ethylhydrazinium hydrogen oxalate (51%); butylamine to butylhydrazinium hydrogen sulfate (49–56%); piperidine to 1-aminopiperidinium hydrogen oxalate (32%); dibutylamine to 1,1-dibutylhydrazinium hydrogen oxalate (34%); trimethylamine to 1,1,1-trimethylhydrazinium hydrogen oxalate (79–85%); 2-picoline to 1-amino-2-methylpyridinium iodide (57%); 2,4-lutidine to 1-amino-2,4-dimethylpyridinium iodide (40%); 2,6-lutidine to 1-amino-2,6-dimethylpyridinium iodide (34%); 2,4,6-collidine to 1-amino-2,4,6-trimethylpyridinium iodide (30%); and quinoline to 1-aminoquinolinium iodide (32%).

Primary, secondary, and tertiary amines can be aminated by chloramine also, but pyridine nitrogens have been aminated only by hydroxylamine-O-sulfonic acid.

It has been shown that, on treatment with base, 1-aminopyridinium iodide undergoes 1,3-dipolar addition with ethyl propiolate or dimethyl acetylenedicarboxylate; thus the N-aminoheterocycles may serve as convenient starting materials for the synthesis of a variety of unusual fused heterocycles.[6]

## References and Notes


1. Institut für Anorganische Chemie der Universität Erlangen, Erlangen, Germany.
2. H. J. Matsuguma and L. Audrieth, *Inorg. Syntheses*, **5**, 122 (1957).
3. A. Meuwsen and R. Gösl, *Angew. Chem.*, **69**, 754, (1957); R. Gösl and A. Meuwsen, *Chem. Ber.*, **92**, 2521 (1959).
4. J. N. Ashley, G. L. Buchanan, and A. P. T. Easson, *J. Chem. Soc.*, **60**, (1947).
5. J. A. Moore, *J. Am. Chem. Soc.*, 77, 3417 (1955); J. A. Moore and J. Binkert, *J. Am. Chem. Soc.*, **81**, 6045 (1959).
6. R. Huisgen, R. Grashey, and R. Krischke, *Tetrahedron Lett.*, 387 (1962).


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

N-(p-acetaminobenzenesulfonimido) pyridine

ethanol (64-17-5)

potassium carbonate (584-08-7)

acetic acid (64-19-7)

potassium sulfate (37222-66-5)

pyridine (110-86-1)

piperidine (110-89-4)

hydriodic acid (10034-85-2)

Quinoline (91-22-5)

2,6-Lutidine (108-48-5)

Butylamine (109-73-9)

methylamine (74-89-5)

Trimethylamine (75-50-3)

chloramine (10599-90-3)

2,4,6-collidine (108-75-8)

2-picoline (109-06-8)

Dimethyl acetylenedicarboxylate (762-42-5)

ethylamine (75-04-7)

1-Aminopyridinium iodide,
Pyridinium, 1-amino-, iodide (6295-87-0)

Hydroxylamine-O-sulfonic acid (2950-43-8)

1-aminopyridinium chloride

ethylhydrazinium hydrogen oxalate

butylhydrazinium hydrogen sulfate

1-aminopiperidinium hydrogen oxalate

Dibutylamine (111-92-2)

1,1-dibutylhydrazinium hydrogen oxalate

1,1,1-trimethylhydrazinium hydrogen oxalate

1-amino-2-methylpyridinium iodide

2,4-lutidine (108-47-4)

1-amino-2,4-dimethylpyridinium iodide

1-amino-2,6-dimethylpyridinium iodide

1-amino-2,4,6-trimethylpyridinium iodide

1-aminoquinolinium iodide

ethyl propiolate (623-47-2)

methylhydrazinium hydrogen sulfate