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.

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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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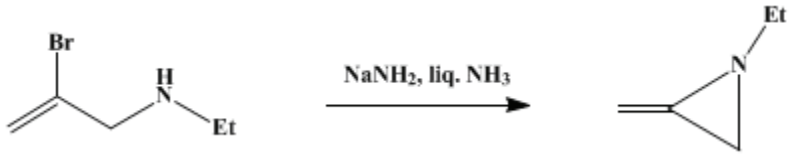
N-ETHYLALLENIMINE

[Aziridine, 1-ethyl-2-methylene-]



Submitted by Albert T. Bottini and Robert E. Olsen[1].
Checked by Thomas H. Lowry and E. J. Corey.

1. Procedure

Caution! This preparation should be carried out in a good hood to avoid exposure to ammonia. The operator should wear rubber gloves and protective goggles because 2-haloallylamines and ethylenimines can cause severe skin and eye irritation.

A 2-l. three-necked flask is fitted with a sealed mechanical stirrer, a gas-inlet tube, and a dry ice condenser protected from the air by a soda-lime drying tube (Note 1). The system is flushed thoroughly with dry ammonia, and 32.8 g. (0.84 mole) of sodium amide (Note 2) is added to the flask. The system is again flushed with ammonia, the condenser is provided with dry ice covered by acetone, and 1.2 l. of liquid ammonia is condensed in the flask. The gas-inlet tube is replaced with a dropping funnel, the stirrer is started, and 118 g. (0.72 mole) of N-(2-bromoallyl)ethylamine[2] is added dropwise in 20–30 minutes; during the addition, the ammonia boils vigorously, and the color of the slurry changes from gray to black. Stirring is continued for 3 hours, and the dry ice is then allowed to evaporate. The condenser is provided with an ice-salt mixture, and the ammonia is allowed to evaporate until the volume is reduced to about 800 ml. (Note 3). Ethanol-free ether (200 ml.) is added rapidly through the dropping funnel, and the reaction is stopped by the slow, dropwise addition (Caution!) of 5 ml. of water. The ammonia is allowed to evaporate overnight. Water (150 ml.) and 100 ml. of ether are added to the residue, and the mixture is stirred for 2 minutes in order to dissolve the precipitated salts. The resulting mixture, which consists of aqueous and ethereal solutions, is separated, and the aqueous phase is extracted with 75 ml. of ether. The ether solutions are combined, dried over sodium hydroxide (Note 4), and distilled through an *efficient* low-holdup column (Note 5). The fraction with b.p. 77–80°, n^{25}D 1.4260–1.4268, which is 96–97% N-ethylallenimine (Note 6), weighs 30–34 g. (48–55%). Pure (>99.5%) N-ethylallenimine has b.p. 77–79°, n^{25}D 1.4281–1.4284 (Note 7) and (Note 8).

2. Notes

1. The glassware should be dried in an oven before use, and water must be rigorously excluded from the reaction mixture.
2. The sodium amide was obtained from Roberts Chemical Co., Nitro, West Virginia.
3. About 1.5–2.5 hours is required; stirring is continued and ice is prevented from forming on the outside of the flask. The checkers used an inner-spiral condenser cooled by ice water.
4. The ether solution and fractions taken during the subsequent distillation may be assayed by gas-liquid partition chromatography on a 0.8-cm. × 200-cm. column heated at 120° and packed with nonyl phthalate supported on ground firebrick.
5. The submitters concentrated the dry ether solution to a volume of 80–100 ml. by distillation through a 1.0-cm. × 40-cm. column packed with glass helices and equipped with a total-reflux head. *p*-Xylene (10 ml.) was added to the residue, and this solution was fractionated through a 0.8-cm. × 30-cm. Podbielniak-type column fitted with a total-reflux head. The submitters recommend that, during distillation of the concentrated solution, a slow stream of nitrogen be passed through the boiling liquid to minimize the formation of dark, tarry products. The checkers used a 1-cm. × 100-cm. spinning-band

column (Nester and Faust Co.) for the distillation of N-ethylallenimine and were able to obtain material of 99% purity (Note 7) directly.
6. This fraction is 2–3% ether, 96–97% N-ethylallenimine, and 1–2% N-ethylpropargylamine. The product from the reaction consists of 80–90% N-ethylallenimine and 10–20% N-ethylpropargylamine. N-Ethylpropargylamine has b.p. 100–102° (760 mm.), n^{25}D 1.4314–1.4316.
7. The submitters obtained essentially pure (>99.5%) N-ethylallenimine by redistilling 30 g. or more of the 96–97% pure product through the Podbielniak column and rejecting the first 10–20% and the last 20% of the distillate. The yield of pure N-ethylallenimine is 18–21 g. (30–35%). Pure N-ethylallenimine has also been obtained in comparable yields by (*a*) distilling the combined concentrated solution from the equivalent of three runs through a 1.3-cm. × 100-cm. column packed with glass helices and equipped with a total-reflux head, and (*b*) treating the crude distillate with lithium aluminum hydride as described for the purification of N-propylallenimine.[3]
8. Samples of pure N-ethylallenimine and other allenimines have been stored at 0° for well over a year with no significant deterioration. *Caution! N-Alkylallenimines, even as dilute solutions in aqueous ethanol, are rapidly destroyed by acid.*[4,5] Therefore concentrated solutions of N-alkylallenimines should not be allowed to come in contact with acid because of the possibilities of violent decomposition.

3. Discussion

The method described is essentially that of Pollard and Parcell.[4] N-Ethylallenimine has been prepared by treating N-(2-bromoallyl)ethylamine in liquid ammonia with sodium amide,[4,6] lithium amide,[6] or potassium amide.[6]

4. Merits of the Preparation

This is a general method for making N-alkylallenimines, and the following ones have been made in this way: N-methyl-,[6] N-propyl-,[6] N-isopropyl-,[4] N-butyl-,[4] N-hexyl-,[6] and N-(3,5,5-trimethylhexyl)-.[4] N-*t*-Butylallenimine[6] and 1-(1-allenimino)-2-hydroxy-3-butene[7] have also been prepared by this method, but with sodium amide/2-bromoallylamine mole ratios of 1.75 and 2.1, respectively. This method has been used for the preparation of pure N-alkylpropargylamines from 2-chloroallylamines.[6,7] The optimum sodium amide/2-chloroallylamine ratio for the preparation of N-alkylpropargylamines is 2.1.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 124

References and Notes

1. Chemistry Department, University of California, Davis, California.
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3. A. T. Bottini and R. E. Olsen, *J. Am. Chem. Soc.*, **84**, 196 (1962).
4. C. B. Pollard and R. F. Parcell, *J. Am. Chem. Soc.*, **73**, 2925 (1951).
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6. A. T. Bottini, B. J. King, and R. E. Olsen, *J. Org. Chem.*, **28**, 3241 (1963).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ethanol (64-17-5)

ammonia (7664-41-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

nitrogen (7727-37-9)

acetone (67-64-1)

p-xylene (106-42-3)

sodium amide (7782-92-5)

lithium aluminum hydride (16853-85-3)

lithium amide (7782-89-0)

potassium amide

2-Bromoallylamine (6943-51-7)

N-(2-Bromoallyl)ethylamine (871-23-8)

N-Ethylallenimine

Aziridine, 1-ethyl-2-methylene- (872-39-9)

nonyl phthalate (24539-59-1)

N-ethylpropargylamine

N-propylallenimine

1-(1-allenimino)-2-hydroxy-3-butene

N-t-Butylallenimine

2-chloroallylamine