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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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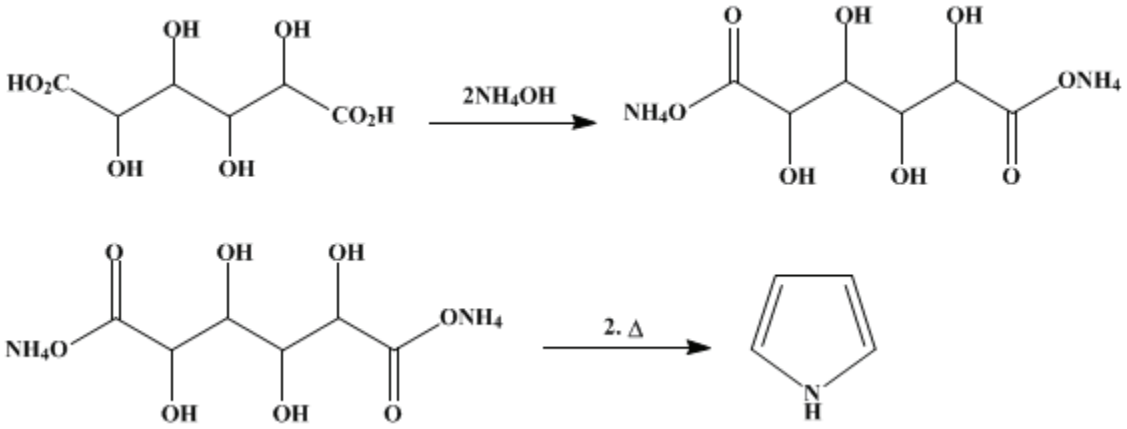
PYRROLE



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1. Procedure

In a 30-cm. evaporating dish or a Pyrex tray are placed 630 g. (3 moles) of mucic acid (Note 1) and 900 cc. of aqueous ammonia (sp. gr. 0.9); this mixture is rapidly stirred to a smooth paste under the hood. The paste is evaporated to complete dryness on a steam bath, and the resulting ammonium mucate is powdered and mixed with 350 cc. of glycerol (Note 2) in a 5-l. round-bottomed Pyrex flask. After standing overnight, the mixture is carefully distilled over a free flame, the heat being applied to one side of the flask alone, so that only a portion of the mass is heated to the reaction temperature. The gases, which are evolved with considerable foaming (Note 3), are led away to a gas trap (Fig. 7, p. 97) or to the open air, on account of their disagreeable nature. The heating is extended throughout the mass as rapidly as appears possible from the state of the mixture. Distillation is continued until a sample of distillate no longer shows oily drops when treated with solid potassium hydroxide; the total volume of distillate amounts to 900–1000 cc.

The entire distillate is redistilled until no further oil separates in the distillate; the watery layer is then separated and returned to the reaction flask, together with the water remaining in the distilling flask. Two liters more of water is added, and about 800 cc. is distilled. The distillate is redistilled until 250–300 cc. has collected in the receiver. This final distillate, on treatment with solid potash, yields a further 2 g. of oil.

The united oil is rapidly dried with a small quantity of solid potassium hydroxide (Note 4) and distilled. The fraction which boils at 127–131° is collected; this is a colorless liquid which darkens on exposure to light (Note 5). The yield is 75–80 g. (37–40 per cent of the theoretical amount).

2. Notes

1. Mucic acid is now manufactured on a large scale by the oxidation of the galactan occurring in certain species of wood.
2. By the use of more glycerol the yield may be slightly increased, but the foaming is very difficult to control. Medicinal mineral oil may be substituted for the glycerol, but the yield is then considerably reduced.
3. Unless the flame is properly adjusted before the foaming becomes very pronounced, there may be difficulty in controlling the distillation. The best method consists in removing the flame from below the flask and allowing it to play on the upper portion of the vessel above the surface of the boiling mixture.
4. When pyrrole is allowed to stand over potassium hydroxide for more than a few hours, combination takes place, lowering the yield.

5. A product of rather better quality, which shows less tendency to darken, may be obtained by finally distilling under reduced pressure. The darkening may also be almost entirely avoided by storing the product in a sealed vessel.

3. Discussion

Pyrrole can be obtained by fractional distillation of bone oil and purification through the potassium derivative.[1] The only synthetic method offering any possibilities involves the thermal decomposition of ammonium mucate, either alone[2] or in the presence of glycerol.[3]

References and Notes

1. Anderson, Ann. **105**, 349 (1858); Weidel and Ciamician, Ber. **13**, 65 (1880); Ciamician and Dennstedt, Ber. **19**, 173 (1886).
2. Schwanert, Ann. **116**, 278 (1860).
3. Goldschmidt, Z. Chem. 280 (1867); Khotinsky, Ber. **42**, 2506 (1909); Blicke and Powers, Ind. Eng. Chem. **19**, 1334 (1927); Andrews and McElvain, J. Am. Chem. Soc. **51**, 887 (1929); Blicke and Blake, ibid. **52**, 235 (1930).

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

ammonium mucate

potash

galactan

ammonia (7664-41-7)

glycerol (56-81-5)

potassium hydroxide (1310-58-3)

Pyrrole (109-97-7)

mucic acid