



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.

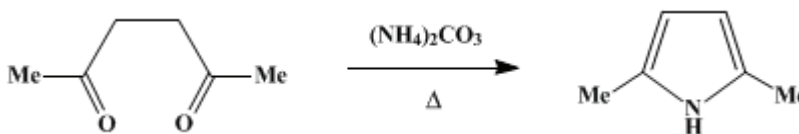
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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2,5-DIMETHYLPYRROLE

[Pyrrole, 2,5-dimethyl-]



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1. Procedure

In a 500-cc. Erlenmeyer flask, fitted with an air-cooled reflux condenser of large bore (Note 1), are placed 100 g. (0.88 mole) of **acetonylacetone** (Note 2) and 200 g. (1.75 moles) of **ammonium carbonate**, in lumps. The mixture is heated in an oil bath at 100° until effervescence stops; this requires sixty to ninety minutes. The air-cooled condenser is replaced by a water-cooled condenser of large bore, and the mixture is refluxed gently at 115° (bath temperature) for thirty minutes longer (Note 1) and (Note 3). The mixture is cooled, and the upper, yellow layer of the pyrrole is separated (Note 4). The lower layer is extracted with 15 cc. of **chloroform**, which is added to the crude pyrrole. The whole is dried over anhydrous **calcium chloride**, in a tightly stoppered container which has been swept out with **nitrogen** beforehand.

The material is transferred (Note 4) to a modified Claisen flask having a fractionating side arm, and the **chloroform** is distilled completely under reduced pressure (without being condensed). The **dimethylpyrrole** is collected at 51–53°/8 mm. or 78–80°/25 mm.; only a small residue (4–5 g., b.p. 80–85°/25 mm.) remains. The product weighs 68–72 g. (81–86 per cent of the theoretical amount) and is quite pure (Note 5); it should be stored in an inert atmosphere in a tightly sealed, dark glass container.

2. Notes

1. Sublimed **ammonium carbonate** must be prevented from blocking the condenser. From time to time the sublimate is pushed back into the reaction mixture by means of a stout glass rod.
2. **Acetonylacetone** may be prepared conveniently by hydrolysis of **2,5-dimethylfuran**. The following procedure is based upon directions supplied to the checkers by Mr. Gwyn Benson, of the Shawinigan Chemicals, Ltd. In a 500-cc. flask are placed 125 g. (1.2 moles) of **2,5-dimethylfuran** (b.p. 93–96°), 60 g. of water, 50 g. of glacial **acetic acid**, and 3 cc. of 10 per cent **sulfuric acid**. The mixture is boiled gently for thirty-six hours, 1 g. of **sodium acetate** crystals is added to convert the **sulfuric acid** to **sodium sulfate**, and the material is distilled at atmospheric pressure through a fractionating column. The fraction boiling up to 155° is removed, and the residual liquid is distilled under reduced pressure. The **acetonylacetone** is collected at 78–79°/15 mm., or 88–89°/25 mm., and weighs 128–133 g. (86–90 per cent of the theoretical amount).
3. At the end of the first and second periods of heating it is well to dissolve the sublimed **ammonium carbonate**, by pouring 5–10 cc. of hot water back and forth through the condenser, and return the solution to the reaction mixture.
4. In this and all the subsequent operations, the **dimethylpyrrole** should be manipulated with a minimum exposure to atmospheric **oxygen**. The distilling apparatus should be swept out with **nitrogen** at the start and **nitrogen** admitted, instead of air, whenever the vacuum is released.
5. Since **2,5-dimethylpyrrole** does not form solid derivatives, the refractive index may be used as a criterion of purity. The value for a freshly distilled specimen is n_D^{25} 1.500. On standing the material gradually turns red and the refractive index rises. This change is accelerated by air and light.

3. Discussion

2,5-Dimethylpyrrole has been prepared by heating acetylacetone with ammonium acetate in glacial acetic acid¹ or with alcoholic ammonia in a sealed tube at 150°. It has also been prepared by hydrolysis and decarboxylation of 2,5-dimethyl-3,4-dicarbethoxypyrrole³ and the monocarbethoxy compound.⁴

References and Notes

1. Ajello and Cusmano, Gazz. chim. ital. **69**, 210 (1939).
 2. Paal, Ber. **18**, 2254 (1885).
 3. Knorr, ibid. **18**, 299, 1565 (1885).
 4. Timoshevskaya, J. Gen. Chem. (U.S.S.R.) **9**, 766 (1939) [C. A. **34**, 423 (1940)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ammonium carbonate (506-87-6)

ammonia (7664-41-7)

ammonium acetate (631-61-8)

sodium acetate (127-09-3)

chloroform (67-66-3)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

nitrogen (7727-37-9)

2,5-Dimethylpyrrole,
Pyrrole, 2,5-dimethyl- (625-84-3)

Acetylacetone (110-13-4)

2,5-dimethylfuran (625-86-5)

2,5-dimethyl-3,4-dicarbethoxypyrrole

dimethylpyrrole

