



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.

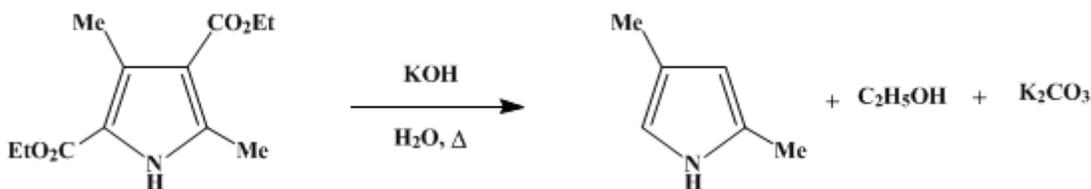
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.217 (1943); Vol. 15, p.20 (1935).

2,4-DIMETHYLPYRROLE

[Pyrrole, 2,4-dimethyl-]



Submitted by Hans Fischer

Checked by C. R. Noller

1. Procedure

A solution of 270 g. (4.8 moles) of potassium hydroxide in 150 cc. of water is prepared in a 3-l. round-bottomed flask, 120 g. (0.5 mole) of crude 2,4-dimethyl-3,5-dicarboxypyrrole (p. 202) and a pinch of sand are added, and the whole is mixed thoroughly by shaking. The flask is fitted with a reflux condenser, and the mixture is heated in an oil bath at 130° for two to three hours with occasional shaking until the thick paste has become partially liquefied owing to the formation of dimethylpyrrole.

The flask is next fitted for distillation with superheated steam and with a separatory funnel for the introduction of water into the center of the flask. A 3-l. round-bottomed flask fitted with a vertical condenser is used as a receiver (*Org. Syn. Coll. Vol. I, 1941, 479*). The temperature of the oil bath is raised to 160°, and superheated steam at 220–250° is introduced. The temperature of the oil bath is then gradually raised to 200°. If foaming becomes too great, a few drops of water are added from the separatory funnel, care being taken that the water does not strike the hot glass walls (*Note 1*). Steam distillation is continued until no more dimethylpyrrole comes over. This takes from one to two hours, and the distillate amounts to 2.5–3 l. The distillate is extracted once with 200 cc. of ether and three times with 100-cc. portions, and the extract is dried for two hours over 20 g. of anhydrous potassium carbonate. The ether is removed by distillation from a 100-cc. modified Claisen flask having a 15-cm. fractionating side arm, the solution being added gradually through a separatory funnel. After the ether is removed the residue is distilled and the fraction boiling at 160–165° is collected. The yield is 27 to 30 g. (57–63 per cent of the theoretical amount) (*Note 2*) and (*Note 3*).

2. Notes

1. If the contents of the flask cake or become semi-solid, the temperature of the oil bath should be lowered and the rate of flow of superheated steam gradually decreased.
2. There is practically no fore-run, but if repeated or larger batches are made it is possible to obtain about 2 g. more of product per run from the higher-boiling fractions. If recrystallized ester is used a higher yield of dimethylpyrrole with less high-boiling products is obtained but the over-all yield is lower.
3. 2,4-Dimethylpyrrole is very readily oxidized in the air to a red resinous substance. If it is not used immediately, it should be stored under nitrogen or sealed in a glass vial under a vacuum.

3. Discussion

2,4-Dimethylpyrrole has been obtained by a large number of reactions, but the method of Knorr¹ and the condensation of acetone with aminoacetone² are the only ones of preparative interest. The procedure given above is one modification of Knorr's method. In another modification, the pyrrole ester and alkali are heated in a steel bomb and the product is distilled in an inert atmosphere; a yield of 95 per cent is reported.³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 198](#)

References and Notes

1. Knorr, Ann. **236**, 326 (1886).
 2. Piloty and Hirsch, *ibid.* **395**, 65 (1913).
 3. Corwin and Krieble, J. Am. Chem. Soc. **63**, 1830 (1941).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[potassium carbonate](#) (584-08-7)

[ether](#) (60-29-7)

[nitrogen](#) (7727-37-9)

[acetone](#) (67-64-1)

[potassium hydroxide](#) (1310-58-3)

[aminoacetone](#) (298-08-8)

[2,4-Dimethylpyrrole,
Pyrrole, 2,4-dimethyl-](#) (625-82-1)

[dimethylpyrrole](#)

[2,4-Dimethyl-3,5-dicarbethoxypyrrole](#) (2436-79-5)