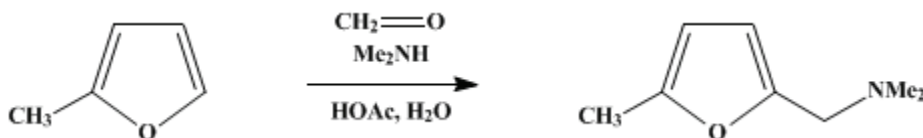


5-METHYLFURFURYL DIMETHYLAMINE

[Furfurylamine, N,N,5-trimethyl-]



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Checked by James Cason, Mary S. Nakata, and William G. Dauben.

1. Procedure

To 200 ml. of glacial acetic acid in a 1-l. round-bottomed flask is added slowly, with cooling in an ice bath, 151 ml. (54 g. of dimethylamine, 1.2 moles) of 40% aqueous dimethylamine solution, followed by 90 ml. (36 g. of formaldehyde, 1.2 mole) of 37% aqueous formaldehyde (formalin) solution. The flask is removed from the ice bath and equipped with a reflux condenser, through which 82 g. (90 ml., 1 mole) of 2-methylfuran (Note 1) is added all at once. Upon gentle swirling of the flask, an exothermic reaction may set in spontaneously; if it does not, the flask is heated on a steam bath until reaction commences. In any event, the spontaneous reaction is allowed to proceed without further external heating. When it ceases, the reaction mixture is heated on a steam bath for another 20 minutes, cooled, and without delay poured into a cold solution of 250 g. of sodium hydroxide (Note 2) in 800 ml. of water.

The reaction mixture is steam-distilled until the distillate is only faintly alkaline (Note 3). To the distillate is added sodium hydroxide (Note 2) to the extent of 10 g. for each 100 ml. of distillate. The strongly alkaline solution is cooled and extracted with two 300-ml. portions of ether. The combined ether layers are dried over 25 g. of solid potassium hydroxide (Note 4), decanted, and concentrated. The residue is distilled under reduced pressure; the yield of 5-methylfurfuryldimethylamine boiling at 62–63°/13 mm. is 96–106 g. (69–76%), n_D^{25} 1.4616–1.4620.

2. Notes

1. The submitters used du Pont 2-methylfuran. Since the stabilizer contained in this material inhibits the reaction, it should be removed before use. The liquid is stored over solid potassium hydroxide (10 g. for each 100 ml. of 2-methylfuran) for 24 hours, decanted, and stored over the same amount of fresh potassium hydroxide at least overnight. A more rapid but less convenient method of removing the stabilizer is to extract the liquid with 10% aqueous potassium hydroxide until the extracts are only faintly colored.
2. The submitters used commercial sodium hydroxide flakes.
3. The steam distillate amounts to 2–3 l.
4. If a large aqueous phase appears, the amine should be decanted and dried further over a fresh portion of potassium hydroxide pellets.

3. Discussion

The first preparation of 5-methylfurfurylamines by the Mannich reaction was by Holdren and Hixon.² The present modification has been published³ without the steam-distillation step, which facilitates separation of the product.

References and Notes

1. University of Notre Dame, Notre Dame, Indiana.

2. Holdren and Hixon, *J. Am. Chem. Soc.*, **68**, 1198 (1946).
 3. Eliel and Peckham, *J. Am. Chem. Soc.*, **72**, 1210 (1950).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

acetic acid (64-19-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

formaldehyde,
formalin (630-08-0)

potassium hydroxide,
potassium hydroxide pellets (1310-58-3)

dimethylamine (124-40-3)

2-methylfuran (534-22-5)

5-Methylfurfuryldimethylamine,
Furfurylamine, N,N,5-trimethyl- (14496-35-6)