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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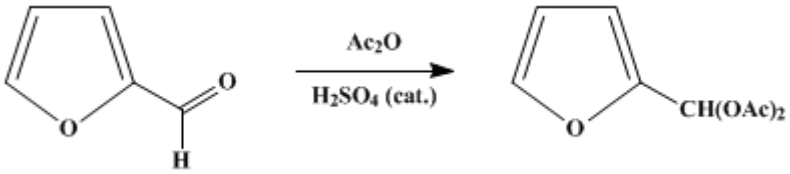
FURFURAL DIACETATE

[2-Furanmethanediol, diacetate]



Submitted by R. T. Bertz[1]
Checked by James Cason, William G. Dauben, W. B. Fearing, and B. P. Summerer.

1. Procedure

In a 300-ml. Claisen flask, whose side neck is elongated by a 10-cm. indented section, 102 g. (1 mole) of acetic anhydride and 0.1 ml. (Note 1) of concentrated sulfuric acid are mixed by hand swirling. The mixture is cooled to 10° by swirling in an ice bath, then there is added, during about 10 minutes, 96 g. (1 mole) of recently distilled furfural (Note 2). The temperature is maintained at 10–20°. After addition is complete and the contents of the flask have been well mixed by swirling, the cooling bath is removed and the reaction allowed to warm up spontaneously. A maximum temperature of about 35° is usually reached in about 5 minutes. After the temperature has dropped to that of the room (20–30 minutes), 0.4 g. (Note 1) of anhydrous sodium acetate is added, the flask is fitted for distillation at reduced pressure, and the mixture is distilled from an oil bath. A fore-run, weighing 50–70 g. and consisting principally of a mixture of acetic anhydride, furfural, and furfural diacetate (Note 3), is collected at 50–140°/20 mm. (Note 4). The product, collected at 140–142°/20 mm., weighs 129–139 g. (65–70%) and melts at 52–53° (Note 4) and (Note 5).

2. Notes

1. In order to freeze the equilibrium during distillation, it is imperative that the sulfuric acid catalyst be previously neutralized by sodium acetate; hence it is important that the small quantities of sulfuric acid and sodium acetate be measured carefully.
2. The furfural used by the checkers was collected at 158–163°. In several runs made with technical grade furfural, which had been stored several years and was black and opaque, a satisfactory product was obtained but yields were 45–53%.
3. This fore-run turns black on standing, but if stored no more than a few days it may be assumed to be an equimolar mixture of furfural and acetic anhydride and may be used as starting material for subsequent runs. If no additional runs are to be made, the yield may be increased by 5–10% by redistilling the fore-run.
4. If collection of the product is started too soon it rapidly darkens and becomes partly liquid on standing. It is advisable to begin collecting the product only after a small sample of distillate, collected separately, sets to a crystalline mass on cooling. Products collected in this manner darkened slightly but remained solid after storage for 2 months. Original distillation of the reaction mixture through a 50-cm. column appeared not to improve the stability to storage, but a sample redistilled in a Claisen flask remained nearly white after storage for 6 months. All stored samples have a strong odor of acetic acid.
5. The submitter has carried out the preparation similarly on a 10-mole scale.

3. Discussion

Furfural diacetate has been prepared from furfural and acetic anhydride in the presence of various catalysts, including cation-exchange resins.[2,3,4,5] It has been claimed that the furfural diacetate preparation of Knoevenagel is improved by the addition of water to the reaction product, followed by ether extraction.[6] The present method is adapted to recovery and reuse of unreacted starting materials.

References and Notes

1. Jacob V. Heemskerklaan 16, Katwyk aan Zee, Holland.
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3. Scheibler, Sotscheck, and Friese, *Ber.*, **57**, 1445 (1924).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

acetic anhydride (108-24-7)

sodium acetate (127-09-3)

Furfural (98-01-1)

Furfural diacetate

2-Furanmethanediol, diacetate (613-75-2)