



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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D-ARABINOSE



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1. Procedure

A solution of 100 g. (0.26 mole) of [pentaacetyl glucononitrile](#) (p. 690) in 150 ml. of [chloroform](#) in a 1-l. Erlenmeyer flask is chilled to -12° . A chilled (-12°) solution of 16 g. (0.7 gram atom) of [sodium](#) in 250 ml. of anhydrous [methanol](#) is added with continual shaking and chilling to the [chloroform](#) solution of the nitrile. The mixture soon solidifies to a pale yellow gelatinous mass. After 10 minutes at -12° this is broken up with a heavy glass rod and dissolved in 600 ml. of a suspension of ice in water. The resulting solution is acidified with an ice-cold mixture of 33 g. (18 ml., 0.32 mole) of 95% [sulfuric acid](#), 5 ml. of [acetic acid](#), and 45 g. of ice. The aqueous layer is separated, washed once with 50 ml. of [chloroform](#), and evaporated without delay ([Note 1](#)) under reduced pressure. The residual heavy syrup is dissolved in 300 ml. of water and again evaporated as completely as possible under reduced pressure, in order to remove residual [hydrogen cyanide](#) ([Note 2](#)). The highly viscous residue, which contains some crystals of [sodium sulfate](#), is dissolved in 500 ml. of hot [methanol](#). After about 10 minutes the [sodium sulfate](#) is filtered with suction and washed with two 25-ml. portions of [methanol](#). The filtrate is concentrated under reduced pressure at 40° to a heavy syrup which is poured while warm into a 200-ml. Erlenmeyer flask. The distilling flask is rinsed twice with 20-ml. portions of hot [ethanol](#), and this rinse is added to the filtrate. The resulting [ethanol](#) solution soon begins to deposit crystals of [arabinose](#); it is stirred by hand during the crystallization and gradually diluted with more [ethanol](#) until 100 ml. in all has been added during the course of an hour. The mixture is allowed to stand for 4–5 hours; the crystals are then filtered, washed with two 25-ml. portions of [ethanol](#), and dried at 40° . The yield of colorless [D-arabinose](#), m.p. 158–158.5°, $[\alpha]_D^{20} -105^\circ$ (final value), is 23.5–26.3 g. (61–68%) ([Note 3](#)).

2. Notes

1. After the reaction mixture has been dissolved in water and acidified, the [hydrogen cyanide](#) should be removed as soon as possible, for the [arabinose](#) tends to react with it even in dilute solution.
2. A slightly higher yield of crystalline [arabinose](#) is obtainable by removing the [hydrogen cyanide](#) with [silver acetate](#). The procedure then consists in acidifying with [acetic acid](#) in place of [sulfuric acid](#), adding an excess of [silver acetate](#), shaking for an hour, filtering, saturating with [hydrogen sulfide](#), again filtering, and adding [sulfuric acid](#) as indicated above. The rest of the procedure is the same. The yield of crystalline [arabinose](#) so obtained is 27.1 g. (70%).
3. A further quantity of [arabinose](#) may be isolated from the mother liquors by the use of [diphenylhydrazine](#): to a solution of 22 g. of [diphenylhydrazine hydrochloride](#) in 100 ml. of absolute [methanol](#) is added a solution of 3.3 g. of [sodium](#) in 50 ml. of [methanol](#). After 15 minutes' standing the [sodium chloride](#) is removed by filtration and washed with [methanol](#). The filtrate, which contains approximately 18 g. of free [diphenylhydrazine](#), is added to the alcoholic mother liquor from the [arabinose](#), and the mixture is inoculated with diphenylhydrazone prepared from some of the crystalline [arabinose](#). The mixture is allowed to stand overnight, and the crystalline diphenylhydrazone is filtered, washed with 95% [ethanol](#), and dried in a vacuum desiccator. In a preparation in which the yield of crystalline [arabinose](#) had been 23.5 g., the yield of diphenylhydrazone was 16.5 g., corresponding to 7.8 g. of the sugar. [Arabinose](#) can be recovered from the diphenylhydrazone by treatment with [formaldehyde](#) in aqueous solution. In view of the high cost of [diphenylhydrazine](#), however, it is doubtful whether its use for this purpose is profitable.

3. Discussion

[D-Arabinose](#) was first prepared by Wohl,¹ by treating [pentaacetyl glucononitrile](#) with ammoniacal

silver nitrate. It has also been obtained from *d*-gluconic acid in various ways: by oxidation of the calcium salt by means of hydrogen peroxide in the presence of ferric acetate;^{2,3,4,5} by boiling an aqueous solution of the mercuric salt;⁶ by electrolysis;⁷ by the action of sodium hypochlorite upon the amide.⁸ It has also been obtained by the electrolytic reduction of D-arabonic acid lactone.⁹ The present method, developed by Zemplén and Kiss,¹⁰ furnishes better yields than that of Wohl.

A modification of the Ruff method,² using ion-exchange resins for the removal of salts, has been published.¹¹

References and Notes

1. Wohl, *Ber.*, **26**, 730 (1893).
 2. Ruff, *Ber.*, **32**, 553 (1899).
 3. Hockett and Hudson, *J. Am. Chem. Soc.*, **56**, 1632 (1934).
 4. Jones, Kent, and Stacey, *J. Chem. Soc.*, **1947**, 1341.
 5. Berezovskii and Kurdyukova, *Zhur. Priklad. Khim.*, **22**, 1116 (1949) [*C. A.*, **45**, 5628 (1951)].
 6. Guerbet, *Bull. soc. chim. France*, (4) **3**, 427 (1908).
 7. Neuberg, *Biochem. Z.*, **7**, 527 (1908).
 8. Weermann, *Rec. trav. chim.*, **37**, 16 (1918).
 9. Swiss pat. 258,581 [*C. A.*, **44**, 4352 (1950)].
 10. Zemplén and Kiss, *Ber.*, **60**, 165 (1927).
 11. Fletcher, Diehl, and Hudson, *J. Am. Chem. Soc.*, **72**, 4546 (1950).
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Appendix

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

diphenylhydrazone

ammoniacal silver nitrate

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

methanol (67-56-1)

formaldehyde (50-00-0)

chloroform (67-66-3)

sodium chloride (7647-14-5)

hydrogen sulfide (7783-06-4)

hydrogen cyanide (74-90-8)

sodium sulfate (7757-82-6)

arabinose,
d-ARABINOSE (28697-53-2)

sodium (13966-32-0)

hydrogen peroxide (7722-84-1)

sodium hypochlorite (7681-52-9)

silver acetate (563-63-3)

pentaacetyl glucononitrile

diphenylhydrazine (530-50-7)

diphenylhydrazine hydrochloride (530-47-2)

ferric acetate

d-arabonic acid lactone

d-gluconic acid (526-95-4)