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.

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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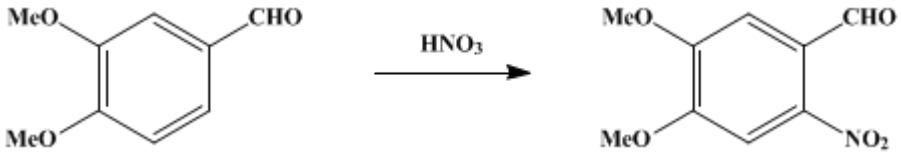
6-NITROVERATRALDEHYDE

[Veratraldehyde, 6-nitro-]



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1. Procedure

The product of this reaction is quite sensitive to light, and the entire procedure should be carried out in semidarkness (Note 1).

A wide-mouth 1-l. Erlenmeyer flask is supported inside a water bath of at least 2-l. capacity so that the bottom of the flask is not in contact with the bottom of the bath. The bath is filled with water at about 15° to cover at least half the height of the flask. The flask is fitted with a moderate-speed stainless-steel propeller-type stirrer, and 350 ml. of nitric acid (sp. gr. 1.4) at 20° is poured into it. Veratraldehyde,[2] 70 g. (0.42 mole) (Note 2), is crushed at least as fine as rice grains and is slowly added in small portions to the acid. The rate of addition should be such that it requires about 1 hour to add all the aldehyde. It is helpful, although not usually necessary, to add two or three ice cubes to the bath at the start of the nitration. The internal temperature is checked from time to time and should be held between 18° and 22°. The mixture is stirred for 10 minutes after the addition of the last of the aldehyde.

The mixture is then poured into 4 l. of vigorously agitated cold water (Note 3) in a suitable opaque container. From this point onward the protection of the product from light is extremely important. The stirring is continued for a few minutes; then the batch is filtered through a 24-cm. Büchner funnel. The container and funnel are kept covered with an opaque sheet of some kind except while the transfer is being made. The cake is sucked down well and then returned to the crock and reslurried a few minutes with 2 l. of cold water. It is then refiltered, pressed out well with a spatula, and drained as well as possible.

The filter cake at this point is 60% to 80% water, and the material is sensitive to heat and to light. The drying, therefore, is difficult and slow, and the exact procedure will depend upon the equipment available. One satisfactory method is to set the Büchner funnel containing the wet material in a large forced-draft oven for 8 hours at 50°. The material, still very wet, is then easily spread on a tray and is placed in a dark but ventilated storeroom, where it is allowed to air-dry for 48 hours or until the weight of the product is less than about 90 g. The product now contains from 10% to 20% of water and is best recrystallized without more thorough drying.

The material is dissolved in 2 l. of boiling 95% ethanol. It is not necessary to filter this solution for the first crystallization. Upon standing overnight, the solution is solid with precipitate. This structure is easily broken up and is filtered on a large Büchner funnel. The mother liquor is concentrated to about 700 ml. and allowed to cool. The second crop of solid is added to the first and dried in a vacuum oven at 50° overnight. The dry material weighs 65–70 g., corresponding to a yield of 73–79%, and melts at 129–131°. It is sufficiently pure for most purposes. One additional crystallization from 1 l. of 95% ethanol gives 55–60 g. of pure material, melting at 132–133°.

2. Notes

1. A sample of 6-nitroveratraldehyde of original melting point 133°, after 9 hours' exposure to the

diffused light of the laboratory, showed a melting point of 88–95°. A small quantity of 6-nitrosoveratric acid, m.p. 185–190°, was isolated from the altered material.
2. The veratraldehyde should have a minimum melting point of 43°. Since there is no difficulty in controlling this reaction, larger batches would undoubtedly be as efficient. The phenomenal bulk of the product and the necessity of minimizing exposure to light make it impractical to handle appreciably more at one time. Smaller batches are perfectly feasible, although it is suggested that for very small amounts of aldehyde somewhat more than the proportional quantity of nitric acid be used. It has been found satisfactory to use 100 ml. of acid with 15 g. of aldehyde.
3. If less water is used, the material is more difficult to break up and wash adequately, and the crude material is more heat-sensitive. Very vigorous agitation is desirable during this precipitation.

3. Discussion

6-Nitroveratraldehyde has always been prepared by direct nitration of the aldehyde. This preparation is a modification of that given by Salway.[3]

References and Notes

1. Cluett, Peabody and Company, Troy, New York.
2. *Org. Syntheses Coll. Vol.* **2**, 619 (1943).
3. Salway, *J. Chem. Soc.*, **95**, 1163 (1909).

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

ethanol (64-17-5)

nitric acid (7697-37-2)

Veratraldehyde (120-14-9)

6-Nitroveratraldehyde,
Veratraldehyde, 6-nitro- (20357-25-9)

6-nitrosoveratric acid