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.

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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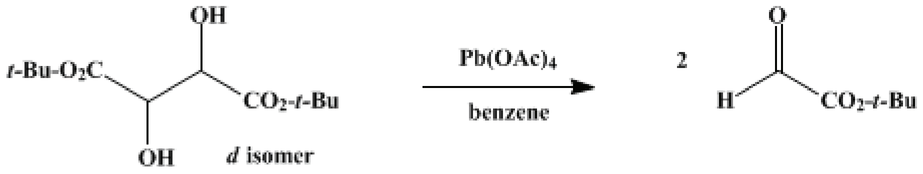
n-BUTYL GLYOXYLATE

[Glyoxylic acid, *n*-butyl ester]



Submitted by Frank J. Wolf and John Weijlard[1].
Checked by N. J. Leonard and L. A. Miller.

1. Procedure

In a 3-l. three-necked round-bottomed flask provided with a Hershberg stirrer and a thermometer are placed 1.25 l. of reagent-grade benzene and 325 g. (1.24 moles) of di-*n*-butyl *d*-tartrate (Note 1). The mixture is stirred rapidly, and 578 g. (1.30 moles) of lead tetraacetate (Note 2) is added over a period of about 25 minutes. The temperature is maintained below 30° by occasional cooling with cold water. After the addition is complete, the mixture is stirred for 1 hour, during which time the gummy salts become crystalline. The salts are removed by filtration with suction and washed with 500 ml. of benzene. The benzene and acetic acid are removed from the filtrate by distillation at 65°/50 mm. The residue is distilled at 20 mm. under nitrogen introduced through an ebullator, using a Vigreux column (2 by 30 cm.), and the fraction boiling between 65° and 79°/20 mm. (main portion at 68–74°) is collected as product. The crude *n*-butyl glyoxylate, which weighs 247–280 g. (77–87%), n_D^{20} 1.442–1.443, d_4^{25} 1.085, is satisfactory for most purposes (Note 3).

2. Notes

1. The di-*n*-butyl *d*-tartrate used was the purest grade from Eastman Kodak Company, m.p. 20–22°.
2. Lead tetraacetate was obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio. It may also be prepared by the procedure described in *Inorganic Syntheses.*[2]
3. The product undergoes autoxidation and should be stored under nitrogen. Further purification may be effected by a second fractional distillation under nitrogen at reduced pressure. The product decomposes on boiling (159–161°) at atmospheric pressure.

3. Discussion

n-Butyl glyoxylate has not been described previously. *Anal.* Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 54.95; H, 7.83. Ethyl glyoxylate has been prepared in good yield by oxidation of ethyl tartrate with red lead oxide[3] or sodium bismuthate.[4] These papers describe isolation of ethyl glyoxylate as carbonyl derivatives.

References and Notes

1. Merck and Company, Rahway, New Jersey.
2. *Inorg. Syntheses*, **1**, 47 (1939).
3. Hamamura, Suzumoto, and Hayashima, *J. Agr. Chem. Soc. Japan*, **22**, 25 (1948) [*C. A.*, **46**, 10108 (1952)].
4. Rigby, *Nature*, **164**, 185 (1949).

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

red lead oxide

acetic acid (64-19-7)

Benzene (71-43-2)

nitrogen (7727-37-9)

Ethyl glyoxylate (924-44-7)

ethyl tartrate

sodium bismuthate (12232-99-4)

n-BUTYL GLYOXYLATE,
Glyoxylic acid, n-butyl ester (6295-06-3)

di-n-butyl d-tartrate

lead tetraacetate (546-67-8)