



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](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.

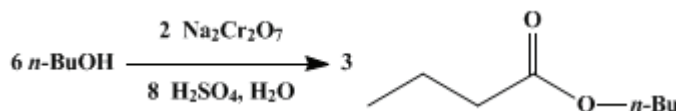
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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 *n*-BUTYRATE**

**[Butyric acid, butyl ester]**



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### **1. Procedure**

In a 2-l. flask fitted with a mechanical stirrer, a thermometer, and a separatory funnel, are placed a cool solution of 240 cc. (4.3 moles) of commercial **sulfuric acid** (sp. gr. 1.84) in 240 cc. of water, and 240 g. (296 cc., 3.24 moles) of technical *n*-butyl alcohol (**Note 1**). The whole is placed in a large, efficient ice-salt bath.

A solution of 320 g. (1.07 moles) of crystalline **sodium dichromate** (350 g. of the ordinary moist technical hydrated salt is also suitable) in 200 cc. of water is dropped from the funnel into the vigorously stirred alcohol mixture as rapidly as can be done without running the temperature above 20°. When most of the **dichromate** has been added, the viscosity of the reaction mixture becomes so great that the stirring is rendered inefficient. The temperature is now allowed to rise to 35° if necessary (**Note 2**), to accelerate the reaction.

The resulting green sirupy emulsion is diluted with an equal volume of water, whereupon 220–225 cc. of an oil containing the desired ester (**Note 3**), slowly separates. This oil is washed three times with water, separated, and treated with a few grams of anhydrous **sodium sulfate** in order to remove most of the water. It is now distilled slowly through a large, efficient fractionating column. The fraction boiling at 150–170° is collected, and should amount to 170–175 cc. It is washed with five 15-cc. portions of 60 per cent **sulfuric acid** (sp. gr. about 1.5) (**Note 4**), is then washed free of acids with dilute **sodium hydroxide**, and finally washed free of alkali with cold water. It is rapidly dried, as before, with **sodium sulfate**, and fractionated through the same distilling column. The fraction boiling at 162–166° (uncorr.) consists of *n*-butyl *n*-butyrate, containing a small percentage of residual **butyl alcohol**. The yield is 96–110 g. (41–47 per cent of the theoretical amount).

If higher purity is desired, the fractionation must be repeated. An additional yield may be secured by further fractionation of the lower-boiling fractions (**Note 5**) and (**Note 6**).

### **2. Notes**

1. When *n*-butyl alcohol is oxidized to **butyric acid** in the presence of a high concentration of **sulfuric acid**, esterification takes place at once, even in the cold, as long as an excess of the **alcohol** is present.
2. If the temperature of the reaction mixture is allowed to rise much above 35°, considerable material escapes in the form of **butyraldehyde** (b.p. 74°).
3. The oil obtained as the first crude product contains, in addition to the desired ester, much unchanged **butyl alcohol**, a little **butyraldehyde**, and a little free **butyric acid**.
4. The 60 per cent **sulfuric acid** is chosen as a wash liquid because it is miscible with **butyl alcohol** but not with the ester. The volatile aldehyde disappears in the two fractionations, while the **butyric acid** is removed by the alkali.
5. The low-boiling fractions could no doubt be returned to a new batch if this process were carried out repeatedly in quantity production. About 25 per cent of the original **butyl alcohol** can be recovered if desired. The very small fractions boiling above 166° may contain esters of other alcohols occurring in the technical product used, and possibly **butyl succinate** and related by-products.
6. It is suggested that improved yields are obtainable when 2 moles of *n*-butyl alcohol are added to 0.62

mole of crystallized [sodium dichromate](#) and 5.1 moles of concentrated [sulfuric acid](#). The temperature is kept between 30° and 40° during the addition, and then the mixture is heated on the steam bath (90–100°) for two to six hours until the supernatant liquid is practically colorless. The mixture is then worked up as described (W. J. Hickinbottom, private communication; <sup>1</sup>).

### 3. Discussion

*n*-Butyl *n*-butyrate can be prepared by the interaction of *n*-butyl alcohol and *n*-butyric acid in the presence of [sulfuric acid](#);<sup>2</sup> by the action of [aluminum butoxide](#) on [butyraldehyde](#);<sup>3</sup> by oxidizing *n*-butyl alcohol with [sodium dichromate](#) and concentrated [sulfuric acid](#);<sup>1</sup> and by oxidizing *n*-butyl alcohol with [sodium chlorate](#) and dilute [sulfuric acid](#) with [vanadium pentoxide](#) as a catalyst,<sup>4</sup> a reaction which may lead to violent explosions if the [sodium chlorate](#) is replaced by [potassium chlorate](#) and if the temperature is not carefully controlled.<sup>5</sup> A number of catalytic procedures, more suitable for industrial than laboratory operation, have been described for preparing *n*-butyl *n*-butyrate by esterification,<sup>6</sup> or from [butyric acid](#) and [hydrogen](#),<sup>7</sup> or from *n*-butyl alcohol alone.<sup>8</sup>

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### References and Notes

1. Reilly and Hickinbottom, Sci. Proc. Roy. Dublin Soc. **16**, 246 (1921).
  2. Gartenmeister, Ann. **233**, 269 (1886).
  3. Skirrow, Can. pat. 279, 974 [C. A. **22**, 2756 (1928)].
  4. Milas, J. Am. Chem. Soc. **50**, 493 (1928).
  5. Wagner, ibid. **50**, 1233 (1928).
  6. Turova, Balandin, Merкурова, and Guseva, J. Applied Chem. (U.S.S.R.) **7**, 1454 (1934) [C. A. **29**, 5814 (1935)].
  7. Kessler Chemical Corp., U. S. pat. 1,997,172 [C. A. **29**, 3686 (1935)].
  8. Koton, J. Gen. Chem. (U.S.S.R.) **6**, 1291 (1936) [C. A. **31**, 1359 (1937)]; Ivannikov, Tsygankova, and Gavrilova, Org. Chem. Ind. (U.S.S.R.) **5**, 53 (1938) [C. A. **32**, 6229 (1938)]; Dunbar, J. Org. Chem. **3**, 242 (1938).
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### Appendix

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

[alcohol](#) (64-17-5)

[sulfuric acid](#) (7664-93-9)

[hydrogen](#) (1333-74-0)

[sodium hydroxide](#) (1310-73-2)

[dichromate](#)

[sodium sulfate](#) (7757-82-6)

[vanadium pentoxide](#)

[butyl alcohol](#),  
[n-butyl alcohol](#) (71-36-3)

Butyric acid, butyl ester,  
n-BUTYL n-BUTYRATE (109-21-7)

sodium dichromate (7789-12-0)

butyric acid,  
n-butyric acid (107-92-6)

butyraldehyde (123-72-8)

butyl succinate (925-21-3)

aluminum butoxide

sodium chlorate (7775-09-9)

potassium chlorate (3811-04-9)