



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.

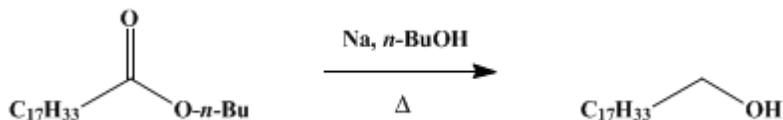
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

Organic Syntheses, Coll. Vol. 2, p.468 (1943); Vol. 15, p.51 (1935).

OLEYL ALCOHOL



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1. Procedure

A 5-l. round-bottomed flask is fitted with a wide-bore Y adapter and two wide-bore reflux condensers. Three liters of anhydrous [butyl alcohol](#) ([Note 1](#)) and 507 g. (1.5 moles) of [butyl oleate](#) ([Note 2](#)) are placed in the flask, and 180 g. (7.8 gram atoms) of clean [sodium](#), cut in approximately 2.5-cm. cubes, is added in one lot and the flask connected to the condensers. The reaction is rather sluggish at first, requiring about one-half hour to reach the boiling point of the [butyl alcohol](#) ([Note 3](#)), but then becomes quite vigorous. With two condensers no difficulty is encountered in taking care of the reflux, but, if the reaction becomes too vigorous or excessive foaming occurs, wet towels should be placed on the flask until the reaction is again under control ([Note 4](#)). Toward the end of the reaction the flask is placed on a heated sand bath and gentle refluxing maintained until all the [sodium](#) has reacted. The heating is stopped temporarily, 160 cc. of water is added gradually through the condenser, and the solution is again refluxed gently for one hour ([Note 5](#)). At the end of this time the heating is stopped and 1.2 l. of water is added. The flask is well shaken and the mixture allowed to separate into two layers. The lower aqueous layer of [sodium hydroxide](#) is siphoned off and discarded ([Note 6](#)) and ([Note 11](#)).

About 200 g. of solid [sodium chloride](#) ([Note 7](#)) is added to the flask, and the [butyl alcohol](#) is removed by steam distillation ([Note 8](#)). The alcohol layer is separated while still hot ([Note 9](#)), transferred to a 1-l. beaker, and heated on a hot plate with stirring until the temperature reaches about 160°. By this time all the water is removed and foaming has stopped ([Note 10](#)). The hot liquid is transferred to a 1-l. Claisen flask having a 25-cm. fractionating side arm, and distilled at 3 mm. After a small fore-run of 5–10 g., the main fraction boils at 177–183°/3 mm. and amounts to 330–340 g. (82–84 per cent of the theoretical amount) ([Note 11](#)).

2. Notes

- Commercial [butyl alcohol](#) is dried by distillation through a 1-m. column, and the portion boiling at 117.5–118.5° is used. The ordinary commercial alcohol is usually sufficiently pure so that the bulk of the alcohol remaining in the flask after the temperature at the top of the column reaches 117° need not be distilled but may be used directly for the reduction.
- The [butyl oleate](#) was prepared by the alcoholysis of 3 kg. of cold-pressed olive oil by refluxing with 7 l. of [butyl alcohol](#) and 150 g. of concentrated [sulfuric acid](#) for 20 hours. The mixture was washed three times with 2.5-l. portions of saturated [sodium chloride](#) solution. During the last washing [methyl orange](#) was added to the solution and enough [sodium carbonate](#) was added to neutralize any acid remaining. The excess [butyl alcohol](#) was distilled and the residue carefully fractionated from a 2-l. Claisen flask having a 25-cm. fractionating side arm. A total of 3075 g. of distilled esters was obtained, of which 2422 g. (about 70 per cent based on the olive oil used) distilled at 204–208°/3 mm. and had approximately the theoretical iodine number. This product contains a small amount of saturated esters, but it is considerably purer than can be obtained from commercial [oleic acid](#) and is satisfactory for most purposes.
- If one wishes to reduce this time, external heat may be applied until the boiling point is reached. In a run in which the [butyl alcohol](#) was heated to boiling before the addition of the [sodium](#), the reaction began more vigorously but the yield was practically unchanged.
- The reaction mixture should not be cooled below the boiling point of the [butyl alcohol](#) as a continuously vigorous reaction is essential for good yields.

5. This saponifies any unreacted ester.
6. The procedure up to this point requires about three and one-half hours and should be continuous.
7. The [sodium chloride](#) prevents the formation of an emulsion during the steam distillation.
8. The [butyl alcohol](#) is readily recovered and dried with very little loss.
9. The soap, and possibly a high-boiling by-product, causes even the liquid alcohols to set to a jelly on cooling.
10. This procedure largely eliminates the difficulty caused by foaming at the start of the vacuum distillation.
11. The procedure as given is generally applicable for the reduction of esters to alcohols in excellent yields. When preparing the solid normal saturated alcohols, the procedure may be modified, if desired, to permit the recovery of the acid from the unreduced ester. After the alkali is removed the alcohol layer is washed with two successive portions of 20 per cent salt solution which are discarded. Neither the strong alkali nor the salt solution removes an appreciable amount of organic acid. A solution of 50 g. of [calcium chloride](#) in 150 cc. of water is added to the [butyl alcohol](#) solution, the mixture is steam-distilled until the [butyl alcohol](#) is removed, and the flask and contents are allowed to cool. A hole is made in the cake of solid alcohol and the water layer removed. Two liters of [toluene](#) is added, and the flask is warmed and shaken until the alcohol dissolves and only fine crystals of the calcium salt of the unreduced acid remain. The solution is cooled to 35° and filtered with suction. The calcium soap is removed from the filter, warmed with about 500 cc. of [toluene](#), cooled, filtered, and washed with a little more [toluene](#). The combined [toluene](#) solutions may be concentrated and the alcohol crystallized, or the [toluene](#) may be completely distilled and the residue vacuum distilled. The insoluble calcium soap may be decomposed, re-esterified, and used in a subsequent reduction.

3. Discussion

Oleyl alcohol has been prepared by the reduction of [ethyl oleate](#) with [hydrogen](#) and a [zinc-chromium oxide](#) catalyst¹ or with [sodium](#) and absolute [ethyl alcohol](#).²

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 671](#)

References and Notes

1. Sauer and Adkins, *J. Am. Chem. Soc.* **59**, 1 (1937).
 2. Bouveault and Blanc, *Bull. soc. chim.* (3) **31**, 1210 (1904). [See the preparation of lauryl alcohol on p. 372 above.](#)
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Appendix

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

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

[calcium chloride](#) (10043-52-4)

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

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

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

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

butyl alcohol (71-36-3)

toluene (108-88-3)

sodium (13966-32-0)

oleic acid (112-80-1)

Oleyl alcohol (143-28-2)

butyl oleate (142-77-8)

ethyl oleate (111-62-6)

zinc-chromium oxide

methyl orange (547-58-0)