



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.

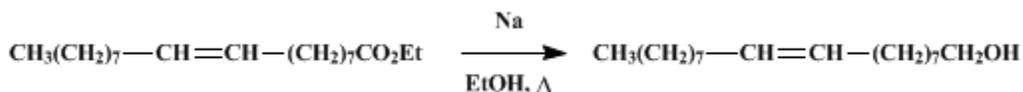
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.671 (1955); Vol. 29, p.80 (1949).

OLEYL ALCOHOL

[9-Octadecen-1-ol]



Submitted by Homer Adkins and R. H. Gillespie.

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1. Procedure

In a 5-l. round-bottomed flask fitted with a large-bore reflux condenser are placed 200 g. (230 ml., 0.65 mole) of **ethyl oleate** (Note 1) and 1.5 l. of absolute **ethanol** (Note 2). Through the reflux condenser is added 80 g. (3.5 gram atoms) of **sodium** rapidly enough to keep up a vigorous reaction. The flask is shaken occasionally. After the initial reaction has subsided, about 200 ml. more of absolute **ethanol** is added, and the mixture is heated on a steam bath until all the **sodium** has reacted. Then 500 ml. of water is added, and the mixture is refluxed for 1 hour to saponify the unreacted ester. The mixture is cooled, and 1.2 l. of water is added. The unsaponifiable fraction is extracted with **ether**, and the extracts are washed with 1% **potassium hydroxide** solution and then with water till free of alkali when tested externally with **phenolphthalein**. The **ether** extract is dried over **sodium sulfate**, the **ether** removed by distillation, and the residue distilled through an efficient column (Note 3). A yield of 84–89 g. (49–51%), b.p. 150–152°/1 mm., is obtained.

Fifty grams of the crude **oleyl alcohol** is crystallized from 400 ml. of **acetone** at –20° to –25° (Note 4) in a jacketed sintered-glass funnel (Note 5). The residue, amounting to about 25 g., is then recrystallized from 250 ml. of **acetone** at –5° (Note 6) to remove saturated alcohols. The **oleyl alcohol** in the filtrate is recrystallized at –60° to –65° (Note 7) and then distilled from a 25-ml. flask with a thermometer well and a low side arm. The yield is 13–16 g., b.p. 148–150°/less than 1 mm.; n_D^{25} 1.4590.

2. Notes

1. The **ethyl oleate** used by the submitters was prepared by esterification of commercial U.S.P. grade **oleic acid** and fractionated through a Widmer column. The fraction boiling at 160–170°/1 mm., n_D^{25} 1.4482–1.4570, iodine value 83.6 (calculated 81.8), was used. The checkers distilled **ethyl oleate** (technical, Eastman Kodak Company) and used the fraction boiling at 164–166°/1 mm., n_D^{25} 1.4522.
2. The purity of the absolute **ethanol** is of prime importance. **Ethanol** dried only by a lime process gives a low yield (20–25%). The **ethanol** used in this procedure was dried over lime and then over **aluminum tert-butoxide**, after which it was distilled directly into the flask used for the reaction.
3. The submitters used a modified Widmer column; the checkers, a Claisen flask modified with a short Vigreux column.
4. The temperature is controlled by selecting a liquid whose freezing point is approximately the temperature at which one wishes to carry out the crystallization, and crushed Dry Ice is added with stirring to keep just a slush. There must be an intimate mixture of solid and liquid at all times. **Carbon tetrachloride** was used for temperatures of –20° to –25°.
5. The apparatus was as follows: A 50-ml. Pyrex sintered-glass funnel, with a sealed-on extension tube, was jacketed with an inverted 500-ml. wide-mouth bottle with the bottom cut off and the edges ground smooth. The jacketed funnel was then placed in a 250-ml. suction flask, the side arm of which was connected to a three-way stopcock. One arm of the stopcock was connected to a water aspirator; the other, to a large test tube (1 1/8 in. by 8 in.) fitted with a two-hole stopper. From the second hole in this stopper was led a tube extending to the bottom of a smaller test tube partly filled with **mercury**. During crystallization, this large test tube was filled three-quarters full of Dry Ice, the **carbon dioxide** gas evolved being allowed to bubble up through the bottom of the sintered-glass funnel. This prevents the

solution from filtering through and also stirs the solution by the rise of small [carbon dioxide](#) bubbles, and hence induces crystallization. The porosity of the sintered-glass funnel is a factor in the size and number of bubbles formed. The mercury trap may be raised or lowered to adjust the pressure, and to act as a vent to prevent the accumulation of [carbon dioxide](#) to give excessive pressures. After crystallization had taken place (about 1 hour) the stopcock was turned to the aspirator and the solution immediately filtered. With this apparatus, about 80 ml. of solution may be crystallized at a time, and no transferring from one container to another is necessary. The checkers found it more convenient to use a 500-ml. sintered-glass funnel along with a proportionally larger bottle, flask, etc. The 400 ml. of [acetone](#) solution was then poured into the funnel in 50-ml. portions with adequate cooling intervals.

6. A crushed ice-salt bath was used.

7. A Dry Ice-chloroform bath was used.

3. Discussion

[Oleyl alcohol](#) has been prepared by the catalytic reduction of [ethyl oleate](#)¹ and heavy-metal oleates;² by the action of [sodium](#) and absolute [ethanol](#) on ethyl³ or butyl⁴ oleate; by the action of [sodium](#) and absolute [butyl alcohol](#) on [butyl oleate](#);⁵ and by the action of [sodium](#) and *tert*-butyl alcohol on [ethyl oleate](#).⁶ The above procedure is essentially that of Kass and Burr,⁷ who prepared [linoleyl alcohol](#). The purification step was derived from the low-temperature crystallization technique of Hartsuch.⁸

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 630](#)

References and Notes

1. Sauer and Adkins, *J. Am. Chem. Soc.*, **59**, 1 (1937).
2. Brit. pat. 584,939 [*C. A.*, **41**, 3812 (1947)].
3. Bouveault and Blanc, *Bull. soc. chim. France*, (3) **31**, 1210 (1904).
4. Palfray and Anglaret, *Compt. rend.*, **224**, 404 (1947); *Bull. mens. ITERG*, 1947, No. 9, 3 [*C. A.*, **42**, 3310 (1948)].
5. *Org. Syntheses Coll. Vol. 2*, 468 (1943).
6. Hausley, *Ind. Eng. Chem.*, **39**, 54 (1947).
7. Kass and Burr, *J. Am. Chem. Soc.*, **62**, 1796 (1940).
8. Hartsuch, *J. Am. Chem. Soc.*, **61**, 1142 (1939).

Appendix

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

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

[ether](#) (60-29-7)

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

[carbon tetrachloride](#) (56-23-5)

[mercury](#) (7439-97-6)

[carbon dioxide](#) (124-38-9)

butyl alcohol (71-36-3)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

phenolphthalein (77-09-8)

oleic acid (112-80-1)

Oleyl alcohol (143-28-2)

butyl oleate (142-77-8)

ethyl oleate (111-62-6)

9-Octadecen-1-ol

linoleyl alcohol (506-43-4)

tert-butyl alcohol (75-65-0)

ALUMINUM tert-BUTOXIDE