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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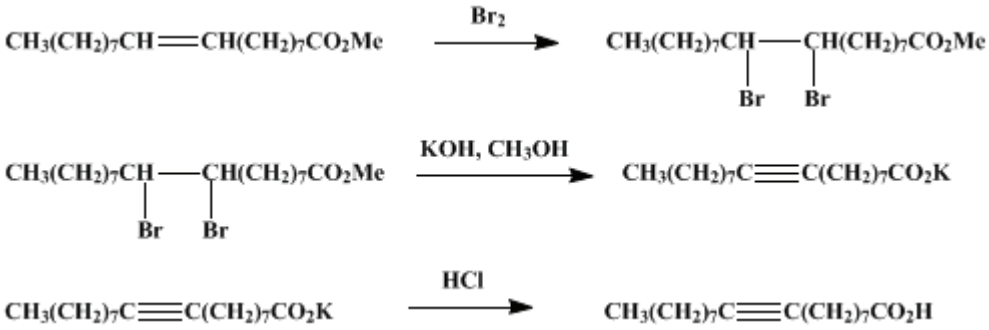
STEAROLIC ACID



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1. Procedure

Bromine is added dropwise with stirring to 35 g. (0.118 mole) of methyl oleate (Note 1) in a 500-ml. round-bottomed flask. The mixture is kept below 50° throughout the addition, which is continued until a slight excess of bromine is present; approximately the theoretical amount (18.9 g.) is decolorized. Methyl oleate (2–3 drops) is then added until the bromine color just disappears. *n*-Amyl alcohol (50 ml.) (Note 2) and potassium hydroxide pellets (40 g., 0.61 mole assuming 85% purity) are added to the flask, and the mixture is heated under reflux for 4 hours in an oil bath at 150°. Then approximately 50 ml. of the *n*-amyl alcohol is distilled at atmospheric pressure (Note 3). The residue on cooling solidifies into a tan-colored mass. Phenolphthalein is added as an indicator, the mixture is cooled in an ice bath, and concentrated hydrochloric acid is added in portions until the red color disappears but reappears on stirring of the viscous mass. This process is continued until the mixture remains colorless. Water (approximately 200 ml.) is added, and the mixture is allowed to come to room temperature. Concentrated hydrochloric acid is added until the mixture is acid to methyl orange. The mixture is again cooled in an ice bath; the oily layer solidifies into a wax, and the acidic water solution is decanted. The wax is dissolved in 100 ml. of 95% ethanol at room temperature, and water is added until the solution becomes turbid. The mixture is heated on a steam bath until a clear solution is formed, and then it is cooled in an ice bath and stirred while the product crystallizes. The semisolid mass is filtered, and the product is recrystallized three times from an ethanol-water mixture. After drying in a vacuum desiccator the yield is 11–14 g. (33–42%), m.p. 46–46.5°; neutral equivalent 279.7–281.4 (calcd. 280.4); hydrogen absorbed by catalytic reduction 94–100%.

2. Notes

1. The methyl oleate was prepared by esterification[1] of commercial U.S.P. grade oleic acid and fractionated through a Widmer column. The fractions used boiled at 140–144°/0.5 mm., 175–179°/2 mm., and had n_D^{25} 1.4500–1.4527 and an iodine number of 93–97 (calcd. 85.6) by iodine bromide titration.[2]
2. *n*-Amyl alcohol was selected as a solvent with a convenient boiling point for the dehydrohalogenation. Acetylenic triple bonds are attacked by water in the presence of strong alkali or strong acid.
3. Part of dehydrohalogenation occurs during the distillation of *n*-amyl alcohol at atmospheric pressure. If the solution was concentrated by distillation under reduced pressure, the product contained bromine and failed to crystallize.

3. Discussion

Stearolic acid has been prepared by the dehydrohalogenation of brominated olive or almond oil,[3] dibromostearic acid,[4] or dichlorostearic acid.[5] The procedure described is a modification of one used by

Kino.[4].

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 851

References and Notes

1. Skraup and Schwamberger, *Ann.*, **462**, 155 (1928).
2. Mahin, *Quantitative Analysis*, 4th ed., pp. 416–420, McGraw-Hill Book Co., New York, 1932.
3. Hoffmann-La Roche, Ger. pat. 243,582 [*Chem. Zentr.*, **1912**, I, 695].
4. Kino, *J. Soc. Chem. Ind. Japan*, **32**, 187 (1929) [*C. A.*, **24**, 1998 (1930)].
5. Inoue and Suzuki, *Proc. Imp. Acad. Tokyo*, **7**, 261 (1931) [*C. A.*, **26**, 87 (1932)].

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

hydrogen (1333-74-0)

bromine (7726-95-6)

potassium hydroxide pellets (1310-58-3)

iodine bromide (7789-33-5)

phenolphthalein (77-09-8)

n-amyl alcohol (71-41-0)

methyl oleate (112-62-9)

oleic acid (112-80-1)

Stearolic acid (506-24-1)

dibromostearic acid

dichlorostearic acid (56279-50-6)

methyl orange (547-58-0)