



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.

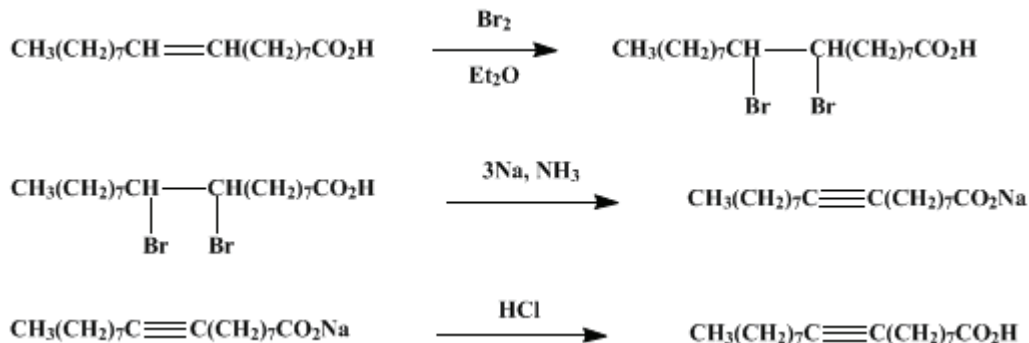
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## STEAROLIC ACID



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### 1. Procedure

**Bromine** is added dropwise with stirring to a solution of 100 g. (0.35 mole) of **oleic acid** of at least 95% purity (**Note 1**) in 400 ml. of dry **ether** maintained at 0–5°, until the color of **bromine** persists. About 53 g. (0.33 mole) of **bromine** is needed; the excess is removed by addition of a few drops of **oleic acid**.

The **sodamide** required for dehydrobromination is prepared<sup>2</sup> in a 5-l. three-necked flask fitted with a sealed Hershberg stirrer, a gas inlet tube, and a large cold-finger condenser charged with Dry Ice-acetone. The condenser outlet is connected to a safety trap followed by a bubbler tube containing concentrated aqueous ammonia. Liquid **ammonia** (1.9 l., (**Note 2**)) is introduced into the flask through the inlet tube (*Hood!*); then 1.6 g. of anhydrous **ferric chloride** (c.p., black) is added in one portion with vigorous stirring. After 5–10 minutes, 3 g. of **sodium** is dropped into the brown solution to convert the iron salt into the catalytic form. After the evolution of **hydrogen** has ceased, the remainder of the **sodium** (total 43 g., 1.87 g. atoms) is added in small pieces with continued stirring. Gray, grainy crystals of sodamide settle out as the reaction proceeds.

The ethereal solution of **dibromostearic acid**, prepared as described above, is introduced slowly from a dropping funnel into the reaction flask. After the reaction has been allowed to proceed for 6 hours with continuous stirring, 60 g. of solid **ammonium chloride** (1.12 moles) is added in portions to destroy excess **sodamide**. The **ammonia** is allowed to evaporate until there remains a dry-appearing solid, and then 1 l. of water is added. The mixture is warmed to 60–70° under **nitrogen** (**Note 3**) and acidified by the addition of an excess (50 ml.) of concentrated aqueous **hydrochloric acid**. The aqueous layer is removed by siphoning, and the organic layer is washed with four 500-ml. portions of hot (60°) water. The aqueous layer is separated each time by siphoning. After the fourth washing, the oily product is solidified by cooling the flask in an ice bath, and the residual water is drained off. The crude product is dried on the steam bath under vacuum (**Note 4**).

The crude acid is dissolved in 500 ml. of petroleum ether at room temperature. The small amount of amorphous solid which may separate is removed by filtration through Supercel, and the filtrate is concentrated under reduced pressure to 300 ml. Chilling to 0–5° yields a first crop of tan crystals which is collected by suction filtration and washed with the minimum amount of ice-cold petroleum ether. Concentration of the mother liquors to 150 ml. and chilling yields a second crop of brownish crystals. The combined crops are dissolved in 300 ml. of petroleum ether, and the light-red solution is chilled to 0–5°. The almost white to light-tan crystals are collected, washed with a small amount of cold petroleum ether, and dried in a vacuum desiccator. There is obtained 51.5–61.5 g. (52–62%) of **stearolic acid**, m.p. 46–46.5° (**Note 5**).

## 2. Notes

1. **Oleic acid** of acceptable purity may be prepared from olive oil fatty acids by the method of Brown and Shinowara,<sup>3</sup> Wheeler and Riemenschneider,<sup>4</sup> Brown and Foreman,<sup>5</sup> or Khan, Deatherage, and Brown.<sup>6</sup> It may also be purchased from the Hormel Institute, Austin, Minnesota.
2. Experience has shown that about 5 g. atoms of **sodium** should be used for each mole of **oleic acid** used as starting material. For each gram atom of **sodium**, 0.8–1.0 g. of **ferric chloride**, 1 l. of liquid **ammonia**, and 0.5–0.7 mole of **ammonium chloride** are necessary. The **sodamide** reaction proceeds best in comparatively dilute liquid **ammonia** solution.
3. The liquid **stearolic acid** is highly susceptible to autoxidation in the presence of air,<sup>7</sup> and this portion of the work-up should be conducted in a **nitrogen** atmosphere.
4. Alternatively, the product obtained after acidification may be taken up in **ether**, and the **ether** extract washed with water, dried over anhydrous **sodium sulfate**, and evaporated to dryness under reduced pressure. This procedure is reported by the submitters to be more convenient for preparations on a smaller scale, and to give a slightly improved yield.
5. This **stearolic acid** has been thoroughly characterized<sup>6</sup> by the freezing-point curve, ultraviolet and infrared spectra, ozonization, and hydrogenation. It has been shown to be free both of positional isomers and of olefinic acids such as oleic and elaidic acids. Its properties include: m.p. 46–46.5°, iodine number (Wijs titration, 30 minutes) 89.5,  $n_D^{54.5}$  1.4510,  $n_D^{61.5}$  1.4484, neutral equivalent 279.2–279.6 (theory 280.4), **hydrogen** uptake 95–100% of theory for a triple bond. The last trace of color is difficult to remove by recrystallization from petroleum ether. It can be removed, however, by crystallization from a 20–30% solution in **acetone** at –5° to –8°, or from an 8–10% solution at –20°, or by distillation (b.p. 189–190° /2mm.).

## 3. Discussion

Nearly all methods for preparation of **stearolic acid** involve dehydrohalogenation of a 9,10-dihalostearic acid, or its esters, with alcoholic **potassium hydroxide**; the most recent method is that of Adkins and Burks.<sup>8</sup> These methods employ drastic conditions, which result in poorer yields than those obtainable on dehydrohalogenation with **sodamide**.<sup>6</sup> **Methyl 9,10-dibromostearate**, on dehydrobromination with **sodamide**, yields **stearolamide**<sup>6</sup> (m.p. 82–83°) which may be hydrolyzed to **stearolic acid**. For preparative purposes, however, this method offers no special advantage over that described here.

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## References and Notes

1. Ohio State University, Columbus, Ohio.
  2. Greenlee and Henne, *Inorg. Syntheses*, **2**, 128 (1946).
  3. Brown and Shinowara, *J. Am. Chem. Soc.*, **59**, 6 (1937).
  4. Wheeler and Riemenschneider, *Oil & Soap*, **16**, 207 (1939).
  5. Foreman and Brown, *Oil & Soap*, **21**, 183 (1944).
  6. Khan, Deatherage, and Brown, *J. Am. Oil Chemists' Soc.*, **28**, 27 (1951); Khan, *J. Am. Oil Chemists' Soc.*, **33**, 219 (1956).
  7. Khan, Brown, and Deatherage, *J. Am. Oil Chemists' Soc.*, **28**, 105 (1951).
  8. *Org. Syntheses Coll. Vol. 3*, 785 (1955).
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## Appendix

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

petroleum ether

9,10-dihalostearic acid  
hydrochloric acid (7647-01-0)  
ammonia (7664-41-7)  
ether (60-29-7)  
ammonium chloride (12125-02-9)  
hydrogen (1333-74-0)  
bromine (7726-95-6)  
sodium sulfate (7757-82-6)  
nitrogen (7727-37-9)  
acetone (67-64-1)  
potassium hydroxide (1310-58-3)  
sodium (13966-32-0)  
ferric chloride (7705-08-0)  
oleic acid (112-80-1)  
sodamide (7782-92-5)  
Stearolic acid (506-24-1)  
dibromostearic acid  
Methyl 9,10-dibromostearate (25456-04-6)  
stearolamide