



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.

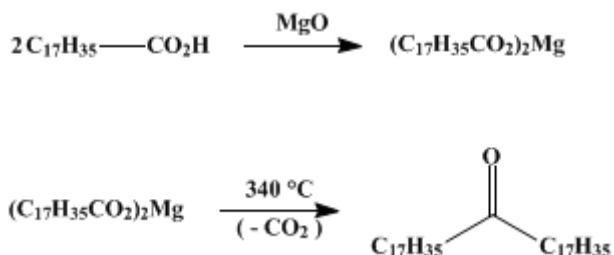
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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STEARONE

[18-Pentatriacontanone]



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1. Procedure

In a 1-l. round-bottomed flask, fitted with a heated reflux condenser maintained at 100–110° (Note 1), are placed 44 g. of *stearic acid* (Note 2) and 20 g. (0.5 mole) of *magnesium oxide* (Note 3). The flask is immersed in a Wood's metal bath heated at 335–340° (Note 4). After the reaction has proceeded for 1 hour, 10-g. portions of melted *stearic acid* are added down the condenser at 15-minute intervals until an additional 240 g. (284 g., 1 mole total) has been added (Note 5). The heating is continued until the total reaction time is 10 hours.

The reaction flask is removed from the metal bath and allowed to cool to about 100°, and the liquid contents are poured with stirring into 1 l. of 4*N* *sulfuric acid* in a 3-l. beaker. This mixture is boiled with vigorous mechanical stirring until the frothing ceases (Note 6) and the upper layer is clear (about 2 hours). The lower aqueous layer is then siphoned off, and the upper layer is boiled for 1 hour with 1 l. of water. The water layer is separated, and the upper layer is boiled with 1 l. of a 5% *sodium hydroxide* solution for 1 hour with vigorous stirring. The ketone layer is then separated and boiled for 1 hour each with three successive 1 l. portions of hot water (Note 7) with good stirring.

The crude *stearone* is allowed to solidify and is then broken up and dried by pressing between filter paper. The crude yield is 230–240 g. (91–95%). The product melts at 84–86° and has an acid value of zero. It is purified by dissolving in 1.2 l. of a 2:1 mixture of *benzene* and absolute *ethanol*, filtering hot, and allowing to crystallize (Note 8). After a second crystallization from the same mixed solvents, the *stearone* is obtained as glistening white flakes, melting clear at 89–89.5° (shrinks at 87–88°). The yield is 204–220 g. (81–87%) (Note 9).

2. Notes

1. The condenser, attached to the flask by a ground-glass joint, is a Pyrex tube 50 cm. long and 20 mm. in internal diameter, wound with No. 26 Nichrome wire covered with asbestos paper. It is connected to a variable transformer and adjusted so as to maintain a temperature of 100–110°. A copper Liebig condenser heated by steam is also suitable provided that the inner tube has a diameter of about 20 mm.

2. The purity and melting point of the final product are dependent on the purity of the *stearic acid*. If Armour's Neo-Fat 1-65, m.p. 64–67° (90–95% *stearic acid*) is recrystallized first from 95% *ethanol* and then from *acetone*, a *stearic acid* melting from 67° to 68° results which yields a *stearone* with a melting point of 88–89° (shrinks at 86–88°).

In order to obtain *stearone* with the highest melting point, the checkers found it necessary to purify the above recrystallized *stearic acid* by converting it to the methyl ester and fractionating this ester under reduced pressure, using a 30-in. electrically heated packed fractionating column. The fraction boiling at 180–182°/4 mm., n_D^{40} 1.4364, is collected. The *methyl stearate* solidifies on cooling and melts at 38–39°. Saponification and acidification yielded white crystals of *stearic acid* melting clear at 69–69.3°

(cor.).

Commercial "stearone" (Armour) is made from Neo-Fat 1-60 (which is approximately 75% stearic and 25% palmitic acid) and melts at 80–84°.

3. Merck's reagent-grade magnesium oxide is suitable. The submitters recommend 10 g. of catalyst, but this amount gave a stearone with m.p. 87–88°. The larger amount, 20 g., gave a product melting clear at 89–89.5°.

4. The temperature of the bath should not be allowed to rise above 345°. Decomposition products are formed which lower the melting point of the final product.

5. With the rate of addition of stearic acid given, the decomposition of magnesium stearate maintains an excess of magnesium oxide in the reaction mixture. Each addition of stearic acid should take 1 to 2 minutes. Thus frothing of the reaction mixture is held under control; a brisk evolution of steam with a little entrained stearic acid follows each addition but quickly subsides and is followed by a steady effervescence due to the liberation of carbon dioxide.

6. A little unchanged magnesium stearate may cause frothing at this stage, which may be controlled by the addition of a few drops of 2-octanol and by vigorous stirring, which hastens decomposition of the soap.

7. The removal of fatty acids from neutral higher aliphatic compounds requires vigorous stirring of the hot aqueous and organic phases.

8. The solubility of stearone falls rapidly with temperature; a hot jacketed funnel is used with gentle suction.

9. This is a general method for the preparation of higher aliphatic ketones. It has been found suitable for the preparation of ketones from fatty acids containing 12 to 20 carbon atoms.

3. Discussion

Stearone has been prepared by heating the alkaline earth salts of stearic acid,² by reaction of liquid stearic acid with iron,^{3,4,5} with alumina,⁶ with manganous oxide and carbonate,⁷ or with magnesium.⁸ It has been prepared by passing stearic acid vapor over various catalysts: manganous oxide,⁹ thoria aerogel,¹⁰ or manganous oxide with chromium sesquioxide.⁹ The literature contains numerous preparations from stearic acid using almost any metal or alkaline-earth oxides. It also has been obtained by the saponification of ethyl α -stearoylstearate with potassium hydroxide.¹¹

Kino¹² studied the reaction of stearic acid with magnesium oxide, with alloys of magnesium, and many other metals, at high temperatures, and obtained stearone. The present method was developed from a reexamination of this reaction.¹³

References and Notes

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

alumina

manganous oxide and carbonate

thoria aerogel

chromium sesquioxide

ethanol (64-17-5)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

magnesium (7439-95-4)

iron (7439-89-6)

carbon dioxide (124-38-9)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

2-Octanol (123-96-6)

magnesium oxide

palmitic acid (57-10-3)

manganous oxide

stearic acid (57-11-4)

Stearone,
18-Pentatriacontanone (504-53-0)

methyl stearate (112-61-8)

magnesium stearate (557-04-0)

ethyl α -stearoyl stearate

