



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.

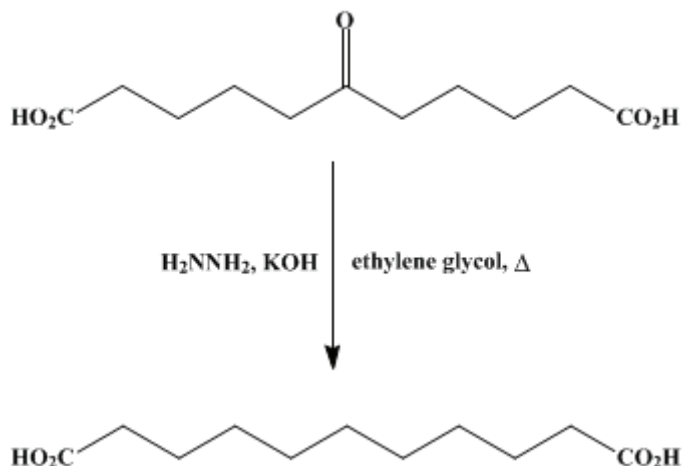
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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HENDECANEDIOIC ACID

[Undecanedioic acid]



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1. Procedure

A 500-ml. round-bottomed flask is attached by a well-lubricated ground-glass joint to a reflux condenser with a side take-off having a stopcock which may be opened to permit distillation. In the flask are placed 170 ml. of commercial **diethylene glycol** and 30 g. (0.46 mole) of **potassium hydroxide** (U.S.P., or reagent grade, 85%). This mixture is heated carefully (*Caution! (Note 1)*) until the **potassium hydroxide** begins to melt and go into solution; then the heat is removed intermittently until the exothermic dissolution is completed. After the solution has been cooled to 80–100°, the condenser is removed and there are added to the flask 35 g. (0.152 mole) of **6-ketoundecanedioic acid** (p. 555) and 22 ml. (22.4 g., 0.38 mole) of commercial 85% **hydrazine hydrate**. The condenser is immediately replaced, and the mixture is warmed cautiously until any exothermic reaction is complete and then heated under reflux for 1 hour.

A thermometer is suspended through the condenser by copper wire so that the bulb is in the heated liquid, the stopcock of the take-off attachment is opened, and the mixture is distilled sufficiently slowly so that the froth does not rise out of the flask. When the liquid temperature has reached 205–210° (after about 30 ml. of distillate has been collected), the stopcock in the takeoff is closed, the thermometer is removed, and the mixture is heated under reflux for 3 hours. If the temperature is checked during this heating period, it is usually found to be in the range 190–200°.

At the end of the heating period the reaction mixture is cooled to about 100–110° (at lower temperatures a gelatinous precipitate separates) and is then poured into 150 ml. of water contained in a 1-l. Erlenmeyer flask. An additional 100 ml. of water is used to rinse the reaction flask. The diluted mixture is acidified to Congo red by slow addition of 6*N* **hydrochloric acid** as the mixture is stirred vigorously to ensure conversion of any precipitated potassium salt to the free acid. The mixture is then cooled by tap water for at least 30 minutes (*Note 2*). The white precipitate is collected by suction filtration, transferred to a beaker, and is heated with about 250 ml. of water until the solid has melted (*Note 3*). As the mixture is cooled, it is stirred vigorously by hand until the oil has resolidified. After the mixture has been cooled again, the precipitated acid is collected by suction filtration, washed with water, and dried (*Note 4*). The yield of **undecanedioic acid**, m.p. 110.5–112° (*Note 5*), is 28.5–30.6 g. (87–93%).

2. Notes

1. When the temperature becomes high enough for the potassium hydroxide to melt under the diethylene glycol, solution occurs rapidly with evolution of heat sufficient to drive material out of the top of the condenser if the source of external heat is not removed immediately. For this reason it is wise not to add the compound being reduced until after solution has been accomplished; moreover, in the case of keto acids there is some evidence that yields are lowered somewhat if the acid is added before solution of the potassium hydroxide. Since diethylene glycol does not present a serious fire hazard, this initial heating is probably best done with a small flame which may be easily removed quickly. Subsequent heating with an electric mantle is recommended.
2. Somewhat higher yields appear to be obtained when the mixture is allowed to stand overnight.
3. Remelting the solid acid over water removes occluded impurities, including salt and diethylene glycol. Moreover, acid which has crystallized in lumps is dried faster than the initial fine precipitate.
4. The submitters suggest recrystallization from benzene as a means of purification.
5. The acid is probably polymorphic,² since the melting point varies somewhat with the rate of heating and a solidified melt remelts more sharply than do the original crystals.

3. Discussion

Hendecanedioic acid has been prepared by hydrolysis of the corresponding dinitrile, obtained from 1,9-dibromononane or 1,9-diiodononane;^{3,4,5} by oxidation of 11-hydroxyhendecanoic acid;^{6,7} by the Arndt-Eistert synthesis from 9-carbethoxynonanoyl⁸ and nonanedioyl chloride;⁹ by the Willgerodt reaction on undecylenic acid;¹⁰ and by treatment of (5,5'-dicarboxy-2,2'-dithienyl)-methane with Raney nickel catalyst and alkali.¹¹ The present method, previously described briefly,^{12,13} appears to represent the most convenient preparation of dibasic acids having an odd number of carbon atoms greater than ten. It has been applied to several other dibasic acids.¹⁴

References and Notes

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(5,5'-dicarboxy-2,2'-dithienyl)-methane

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

Raney nickel (7440-02-0)

potassium hydroxide (1310-58-3)

hydrazine hydrate (7803-57-8)

1,9-dibromononane (4549-33-1)

diethylene glycol (111-46-6)

9-carbethoxynonanoyl chloride

Hendecanedioic acid,
Undecanedioic acid (1852-04-6)

6-Ketohendecanedioic acid (3242-53-3)

1,9-diiodononane (24613-65-8)

11-hydroxyhendecanoic acid (3669-80-5)

nonanedioyl chloride (123-98-8)

undecylenic acid (112-38-9)