



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.

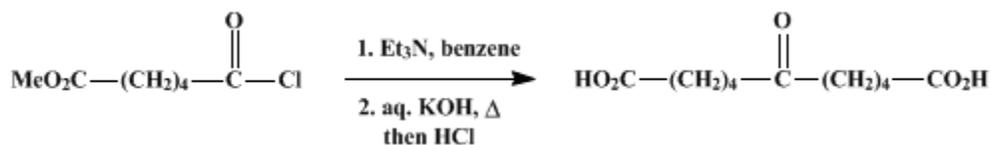
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.555 (1963); Vol. 38, p.38 (1958).

6-KETOHENDECANEDIOIC ACID

[Undecanedioic acid, 6-oxo-]



Submitted by Lois J. Durham, Donald J. McLeod, and James Cason¹.

Checked by N. J. Leonard, D. H. Dybvig, and K. L. Rinehart, Jr..

1. Procedure

In a 1-l. three-necked flask fitted with a sealed mechanical stirrer, a 125-ml. dropping funnel, a thermometer, and a drying tube filled with calcium chloride, are placed 500 ml. of dry benzene (Note 1) and 89.3 g. (0.5 mole) of δ -carbomethoxyvaleryl chloride (Note 2). The thermometer is adjusted to extend into the stirred liquid but not into the path of the stirrer. The mixture is cooled, with stirring, to 3–5° in an ice bath, then 50.6 g. (0.5 mole) of triethylamine (Note 3) is added as rapidly as is consistent with keeping the temperature of the reaction mixture below 25° (3–5 minutes). When the mildly exothermic reaction has subsided, the ice bath is removed and a warm water bath is used to raise the temperature of the reaction mixture to 33–35° during 10–15 minutes. A heavy white precipitate of triethylamine hydrochloride separates. After the reaction mixture has been warmed to about 35°, the water bath is removed and stirring is continued without heating for 30 minutes.

The reaction mixture is filtered (Note 4) with suction, and the amine salt is washed with about 200 ml. of benzene. The filtrate and washings are combined and transferred to a 1-l. round-bottomed flask, benzene is removed at reduced pressure, and to the residue is added 500 ml. of 2*N* aqueous potassium hydroxide. This mixture is heated under reflux for 4 hours, by which time the solution should become completely homogeneous. The cooled solution is extracted with three 100-ml. portions of ether, then acidified to Congo red with concentrated hydrochloric acid (approximately 95 ml.). After the solution has been cooled in ice for at least 1 hour, the precipitated white solid is collected by suction filtration, washed with water, and recrystallized from a minimal amount of hot water (105–125 ml. required at about 90°). The yield of colorless 6-ketohendecanedioic acid, m.p. 108–109° (Note 5) is 35–37 g. (60–64%).

2. Notes

1. A quantity of thiophene-free benzene is conveniently dried by distilling about one-fourth of it, then cooling the residue with protection from moisture by use of a calcium chloride tube.
2. This ester acid chloride is prepared by allowing 100 g. (0.63 mole) of redistilled commercial methyl hydrogen adipate (b.p. 155–156°/7 mm., 172–173°/13 mm.) to stand overnight at room temperature with 150 g. (1.25 moles) of thionyl chloride. A Claisen head is attached, and the thionyl chloride is removed at aspirator pressure on a steam bath. A pump is attached, and the ester acid chloride is distilled; the yield is at least 94 g. (84%), b.p. 114–115°/1 mm.
3. Triethylamine purified by drying over sodium hydroxide pellets and distilling from α -naphthyl isocyanate was found to give no better results than amine which had been distilled through a half-meter Vigreux column and collected over the range 89.5–90°.
4. Frequently the flocculent precipitate of triethylamine hydrochloride is filtered with some difficulty; accordingly, a sufficiently large Büchner funnel should be used for the filtration.
5. Titration of this acid gives an equivalent weight in the range 115–116 (theory, 115). The highest melting point recorded for this acid is 111°.²

3. Discussion

6-Ketohendecanedioic acid has been prepared by the reactions described,^{3,4} by the dialkylation of diethyl acetonedicarboxylate with ethyl γ -iodobutyrate in the presence of sodium ethoxide followed by hydrolysis and decarboxylation,^{2,5} and by the permanganate oxidation of 6-(1'-cyclohexenyl)-1-hexene,⁶ by the reaction of 1-morpholinocyclohexene with glutaryl chloride in the presence of triethylamine,⁷ and by hydrolysis of the reaction product obtained by treating bromomagnesium cyclopentanone-2-carboxylate with adipyl chloride.⁸ The present method is a simplification of the procedure originally described by Sauer.³ This method is practical for the preparation of symmetrical keto dibasic acids and esters.⁹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 510](#)

References and Notes

1. University of California, Berkeley, California.
 2. English, *J. Am. Chem. Soc.*, **63**, 941 (1941).
 3. Sauer, *J. Am. Chem. Soc.*, **69**, 2444 (1947).
 4. Cason, Taylor, and Williams, *J. Org. Chem.*, **16**, 1187 (1951).
 5. Leonard and Goode, *J. Am. Chem. Soc.*, **72**, 5404 (1950).
 6. Kreuchunas, *J. Am. Chem. Soc.*, **75**, 4278 (1953).
 7. Hünig and Lücke, *Chem. Ber.*, **92**, 652 (1959).
 8. Plesek, *Chem. listy*, **49**, 1840 (1955) [*C. A.*, **50**, 9294 (1956)].
 9. Blomquist, Johnson, Diuguid, Shillington, and Spencer, *J. Am. Chem. Soc.*, **74**, 4203 (1952).
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Appendix

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

[calcium chloride](#) (10043-52-4)

[hydrochloric acid](#) (7647-01-0)

[Benzene](#) (71-43-2)

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

[sodium hydroxide](#) (1310-73-2)

[thionyl chloride](#) (7719-09-7)

[potassium hydroxide](#) (1310-58-3)

[sodium ethoxide](#) (141-52-6)

[Triethylamine hydrochloride](#) (554-68-7)

[adipyl chloride](#) (111-50-2)

[methyl hydrogen adipate](#) (627-91-8)

α -naphthyl isocyanate (86-84-0)

triethylamine (121-44-8)

6-Ketohendecanedioic acid,
Undecanedioic acid, 6-oxo- (3242-53-3)

δ -carbomethoxyvaleryl chloride (35444-44-1)

diethyl acetonedicarboxylate (570-08-1)

ethyl γ -iodobutyrate (7425-53-8)

1-morpholinocyclohexene (670-80-4)

glutaryl chloride (2873-74-7)

bromomagnesium cyclopentanone-2-carboxylate

6-(1'-cyclohexenyl)-1-hexene