



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.

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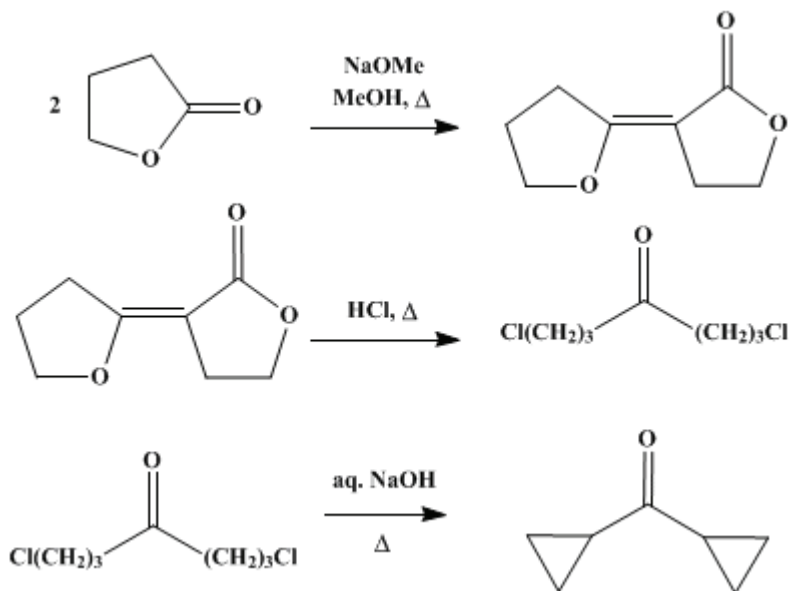
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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DICYCLOPROPYL KETONE

[Ketone, dicyclopropyl]



Submitted by Omer E. Curtis, Jr., Joseph M. Sandri, Richard E. Crocker, and Harold Hart¹.
Checked by V. Boekelheide, R. Taber, and D. S. Tarbell.

1. Procedure

A solution of sodium methoxide is prepared from 50 g. (2.17 g. atoms) of freshly cut sodium and 600 ml. of absolute methanol (Note 1) in a 3-l. three-necked flask placed on a steam bath and equipped with a sealed stirrer (Note 2), dropping funnel, and a condenser set downward for distillation (Note 3). To the stirred solution is added in one portion 344 g. (4.0 moles) of γ -butyrolactone (Note 4), and the flask is heated until methanol distils at a rapid rate. After 475 ml. of methanol is collected, a filter flask or other suitable device equipped with a side arm is connected to the condenser. This receiver is surrounded by an ice bath, and reduced pressure from an aspirator is applied cautiously (frothing) with continuous stirring. An additional 50–70 ml. of methanol is collected in this way. The residue presumably is dibutyrolactone (Note 5).

The condenser is set for reflux, and the steam bath is replaced with a more potent source of heat (electric heating mantle, oil bath, or direct flame). Concentrated hydrochloric acid is added with stirring, cautiously at first because a considerable amount of carbon dioxide is evolved. A total of 800 ml. of acid is added in about 10 minutes (Note 6). The mixture is heated under reflux with stirring for 20 minutes, then cooled in an ice bath (Note 7). A solution of 480 g. of sodium hydroxide in 600 ml. of water is added to the stirred mixture as rapidly as possible, without allowing the temperature to go above 50° (Note 8). The mixture is then heated under reflux for an additional 30 minutes.

The condenser is arranged for downward distillation, and a total of 650 ml. of ketone-water mixture is collected as distillate. Sufficient potassium carbonate is added to saturate the aqueous layer, and about 130 ml. of ketone is separated. The aqueous layer is extracted with three 100-ml. portions of ether, and the combined ether and ketone layers are dried over 25 g. of anhydrous magnesium sulfate. The product remaining after removal of the ether is distilled through an efficient column. The yield of dicyclopropyl ketone boiling at 72–74°/33 mm., n_D^{25} 1.4654, is 114–121 g. (52–55%) (Note 9).

2. Notes

1. Commercial [sodium methoxide](#) (117 g.) in 520 ml. of [methanol](#) may be used instead of metallic [sodium](#).
2. The stirrer should be sturdy and capable of giving vigorous agitation.
3. It is desirable to have the condenser arranged for reflux during preparation of the methanolic [sodium methoxide](#), if it is made from [sodium](#) metal.
4. Commercial lactone (available from General Aniline and Film Corporation, 435 Hudson Street, New York 14, New York) should be redistilled, b.p. 88–90°/12 mm., before use.
5. Dibutyrolactone can be isolated as a crystalline solid, m.p. 86–87°, from this residue.² The preparation can be interrupted at this point without jeopardizing the yield.
6. The color of the mixture changes from yellow through dark orange to dark reddish brown.
7. At this point, the following procedure may be used to prepare [1,7-dichloro-4-heptanone](#). To the cooled, stirred solution is added 200 ml. of [ether](#), which brings the dense dichloroketone to the upper layer. The latter is separated, and the acid layer is extracted with two 100-ml. portions of [ether](#). The combined [ether](#) layers are dried over 25 g. of anhydrous [calcium chloride](#). After removal of the solvent, the residue is distilled through an efficient column. The yield of [1,7-dichloro-4-heptanone](#), b.p. 106–110°/4 mm., n_D^{25} 1.4713, is 263–278 g. (72–76%). The material takes on a purple cast rapidly and should be stored in a refrigerator.
8. Considerable salt separates at this point but does not interfere with the subsequent steps.
9. According to the submitters, a similar procedure can be applied to substituted lactones; [di-\(2-methylcyclopropyl\) ketone](#), b.p. 65–67°/7 mm., n_D^{25} 1.4600, has been made from [γ-valerolactone](#) in 50% yield.

3. Discussion

This procedure is a modification of one recently described in the literature.³ The first step is based on early work of Fittig⁴ and Volhard⁵ as modified by Spencer and Wright.² The third step, ring closure of a γ -haloketone,⁵ is well known (p.597). [Dicyclopropyl ketone](#) was reported to form in small amounts from the decarboxylation of [cyclopropanecarboxylic acid](#) over thoria,⁶ but there is some doubt³ about the product.

References and Notes

1. Michigan State University, East Lansing, Michigan.
2. Spencer and Wright, *J. Am. Chem. Soc.*, **63**, 1281 (1941).
3. Hart and Curtis, Jr., *J. Am. Chem. Soc.*, **78**, 112 (1956).
4. Fittig, *Ann.*, **256**, 50 (1889); Fittig and Stöm, *Ann.*, **267**, 191 (1892).
5. Volhard, *Ann.*, **267**, 78 (1892).
6. Michiels, *Bull. soc. chim. Belges*, **24**, 396 (1910) [*Chem. Zentr.*, **82**, I, 66 (1911)].

Appendix

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

thoria

dibutyrolactone

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

[potassium carbonate](#) (584-08-7)

hydrochloric acid (7647-01-0)

methanol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

carbon dioxide (124-38-9)

sodium methoxide (124-41-4)

sodium (13966-32-0)

Dicyclopropyl ketone,
Ketone, dicyclopropyl (1121-37-5)

γ -butyrolactone (96-48-0)

1,7-Dichloro-4-heptanone (40624-07-5)

di-(2-methylcyclopropyl) ketone

γ -valerolactone (108-29-2)

magnesium sulfate (7487-88-9)

Cyclopropanecarboxylic acid (1759-53-1)