



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.

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.

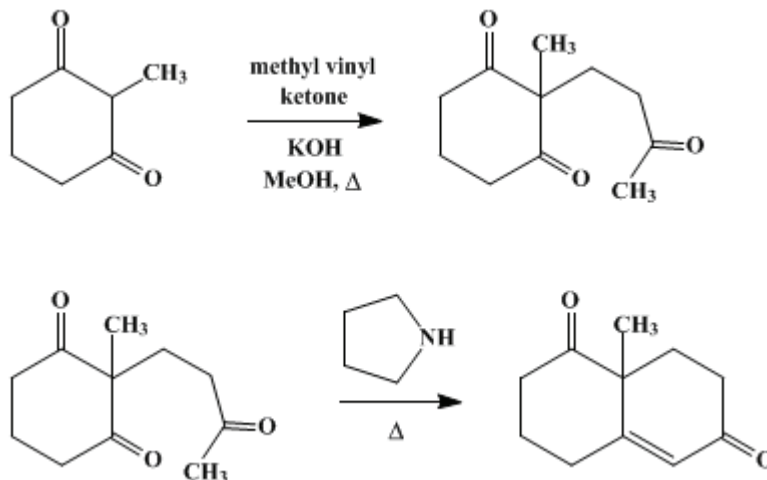
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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. 5, p.486 (1973); Vol. 41, p.38 (1961).*

## 1,6-DIOXO-8a-METHYL-1,2,3,4,6,7,8,8a-OCTAHYDRONAPHTHALENE

[1,6-Naphthalenedione, 1,2,3,4,6,7,8,8a-octahydro-8a-methyl-]



Submitted by S. Ramachandran and Melvin S. Newman<sup>1</sup>.  
Checked by Max Tishler, G. A. Stein, and G. Lindberg.

### 1. Procedure

A mixture of 63.1 g. (0.5 mole) of 2-methyl-1,3-cyclohexanedione (Note 1), 52.6 g. (0.75 mole) of methyl vinyl ketone (Note 2), about 0.25 g. (3 pellets) of potassium hydroxide, and 250 ml. of absolute methanol is placed in a 500-ml. round-bottomed flask fitted with a reflux condenser and a drying tube (Note 3). The mixture is heated under reflux for 3 hours, and the dione gradually goes into solution. At the end of this period, methanol and the excess methyl vinyl ketone are removed by distillation under reduced pressure (Note 4) and (Note 5). The residual liquid is dissolved in 250 ml. of benzene, a Dean-Stark phase-separating head is attached, and 20 ml. of solvent is removed by distillation at atmospheric pressure to remove traces of water and methanol. The solution is cooled well below the boiling point, 3 ml. of pyrrolidine is added (Note 6) and the mixture held at reflux for about 30 minutes, during which time about 9 ml. of water collects in the trap. Refluxing is continued for an additional 15 minutes after the separation of water ceases. The water collected is removed, and then 50 ml. of solvent is distilled. The reddish reaction mixture is cooled to room temperature and diluted with 150 ml. of ether. This solution is washed with 100 ml. of distilled water containing 15 ml. of 10% hydrochloric acid and 100 ml. of water. The aqueous extracts are extracted with 50 ml. of ether (Note 7), and the combined organic layers are washed with three 100-ml. portions of water, then with saturated salt solution and dried over magnesium sulfate. The solvents are then removed, and on distillation of the residue (82–85 g.) (Note 8) at 0.5–1.0 mm. (Note 9) the material, b.p. 117–145°, is collected and diluted with 5 ml. of ether. The distillate is placed overnight in a refrigerator, the resulting crystals are then collected by rapid filtration and washed with about 25 ml. of cold ether (Note 10) and (Note 11). The first crop of diketone weighs 50–53 g. and is colorless. The combined mother liquors are redistilled to obtain a further 4–6 g. of crystalline product. A yield of 56–58 g. (63–65% based on dione) of 1,6-dioxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene, m.p. 47–50°, suitable for most other purposes, is obtained (Note 12).

### 2. Notes

1. The 2-methyl-1,3-cyclohexanedione was prepared by the method described by Mekler et al., this volume, p. 743.

2. Technical grade [methyl vinyl ketone](#) supplied by Matheson, Coleman and Bell Co., Cincinnati, Ohio, was used without further purification.
3. The checkers found that stirring during reflux and concentration and in the cyclization step was advantageous.
4. The submitters report that the intermediate 2-methyl-2-(3'-oxobutyl)-1,3-cyclohexanedione can be isolated in 85% yield<sup>2</sup> at this point if desired.
5. The checkers removed [methanol](#) and [methyl vinyl ketone](#) at 650 mm. pressure with a water bath at 70°.
6. On adding [pyrrolidine](#) an exothermic reaction occurs rapidly. Cooling is needed to prevent too rapid a reaction. The submitters report that [piperidine](#) may be used in place of [pyrrolidine](#).
7. The checkers extracted the aqueous extracts twice with 75-ml. portions of [ether](#).
8. The checkers found the residual weights to amount to 87–100 g.
9. The checkers used a saddle-packed 5-in. column and found b.p. 137–150°/0.6–0.7 mm.; 123–150°/0.2–0.5 mm.; and 132–141°/0.5–0.8 mm.
10. A successful crystallization yields relatively large crystals which may be rapidly filtered and washed with [ether](#) with little loss. If fine crystals are obtained, it is preferable to redissolve and allow the material to crystallize again.
11. Because of the high solubility in ether (1 g. per 2.5 ml. at room temperature), the checkers washed the product with [hexane](#) (b.p. 60–71°).
12. Purer product, m.p. 48.6–50.0°, may be obtained by crystallization from [ether](#).

### 3. Discussion

1,6-Dioxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene has been obtained through the reaction of 2-methyl-1,3-cyclohexanedione with [acetonedicarboxylic acid](#) and [formaldehyde](#),<sup>3</sup> [4-diethylamino-2-butanone methiodide](#),<sup>3</sup> [pyridine](#) and [4-diethylamino-2-butanone](#),<sup>4</sup> [triethylamine](#) and [4-diethylamino-2-butanone](#),<sup>5</sup> and by cyclization of 2-methyl-2-(3-oxobutyl)-1,3-cyclohexanedione using either [aluminum tert-butoxide](#) or [piperidine phosphate](#) as catalyst.<sup>6,7</sup>

### 4. Merits of Preparation

1,6-Dioxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene has been employed as an intermediate in the synthesis of terpenes<sup>8,9</sup> and in the projected synthesis of steroids.<sup>4,10</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 7, 368](#)

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### References and Notes

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

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

Acetonedicarboxylic acid

formaldehyde (50-00-0)

pyridine (110-86-1)

potassium hydroxide (1310-58-3)

piperidine (110-89-4)

4-diethylamino-2-butanone (3299-38-5)

magnesium sulfate (7487-88-9)

pyrrolidine (123-75-1)

hexane (110-54-3)

methyl vinyl ketone (78-94-4)

triethylamine (121-44-8)

1,6-DIOXO-8a-METHYL-1,2,3,4,6,7,8,8a-OCTAHYDRONAPHTHALENE,  
1,6-Naphthalenedione, 1,2,3,4,6,7,8,8a-octahydro-8a-methyl- (20007-72-1)

2-Methyl-1,3-cyclohexanedione (1193-55-1)

2-Methyl-2-(3-oxobutyl)-1,3-cyclohexanedione (5073-65-4)

piperidine phosphate

ALUMINUM tert-BUTOXIDE

4-diethylamino-2-butanone methiodide