



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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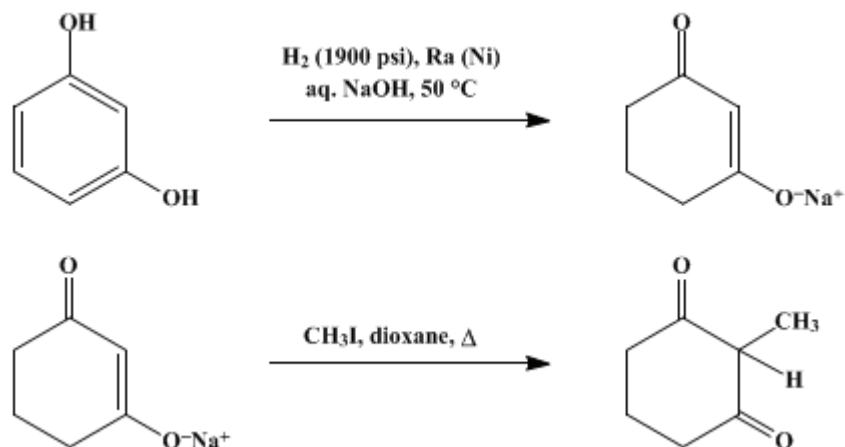
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.743 (1973); Vol. 41, p.56 (1961).

2-METHYL-1,3-CYCLOHEXANEDIONE

[1,3-Cyclohexanedione, 2-methyl-]



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1. Procedure

A freshly prepared solution of 96.0 g. (2.4 moles) of sodium hydroxide, 335 ml. of water, and 220.2 g. (2.0 moles) (Note 1) of resorcinol (Note 2) is placed in a 1.3-l. hydrogenation bomb together with 40.0 g. of finely powdered nickel catalyst (Note 3). The hydrogenation is carried out under an initial pressure of about 1900 lb. of hydrogen with agitation. The reaction is slightly exothermic, and gentle heating is applied to maintain a temperature of 45–50° (Note 4). The hydrogenation is continued until about a 10% excess of the theoretical amount of hydrogen (2.0 moles) has been absorbed (Note 5). At this point, the agitation is stopped, and the bomb is cooled to room temperature. The reaction mixture is poured into a 1-l. beaker, and the catalyst is removed by filtration with the aid of three 50-ml. portions of water for the combined operations. The filtrate and washings are transferred to a 2-l. round-bottomed flask and treated with 33.5 ml. of concentrated hydrochloric acid (for partial neutralization), 145 ml. of dioxane, and 335 g. (2.4 moles) of methyl iodide (Note 6). The reaction mixture is refluxed for a total of 12–14 hours. After 7 or 8 hours, an additional 33.5 g. (0.24 mole) of methyl iodide is added. The system is cooled several hours in an ice bath, and the 2-methyl-1,3-cyclohexanedione which crystallizes is collected by filtration (Note 7), washed with four 200-ml. portions of cold water (Note 8), and then dried in an oven at 110°. The initial crop of dione, m.p. 206–208° dec., weighs 138–142 g. (54–56%). The mother liquors are concentrated under reduced pressure to one-half of their original volume and are then cooled in an ice-salt bath to yield an additional 7–11 g. (3–5%) of slightly yellow dione which melts at 200–204° dec.

The 2-methyl-1,3-cyclohexanedione thus obtained (Note 9) can be purified by recrystallization from 95% ethanol, using about 20 ml. of ethanol for each 5 g. of product to give colorless crystals, m.p. 208–210° dec., with only minor loss of material.

2. Notes

1. The submitters have carried out runs with as much as 990 g. (9.0 moles) of resorcinol.
2. Both Merck resorcinol U.S.P. powder and resorcinol of practical grade give satisfactory results.
3. Many different nickel catalysts have been used: e.g., Grade 0140T1/8 Harshaw Chemical Co., Cleveland 6, Ohio; reduced Universal Oil Products hydrogenation catalyst pellets which are pulverized just before use; and Raney nickel catalyst W-2. Before using the Raney nickel, care must be taken to free it of aluminum by careful washing with 5% sodium hydroxide solution, followed by thorough

rinsing with distilled water (private communication from Dr. Richard Weiss, van Ameringen-Haebler, Inc., New York 19, N. Y.). The checkers prepared Raney nickel catalyst W-2 according to the procedure in *Org. Syntheses*, Coll. Vol. 3, 181 (1955).

4. The temperature should not exceed 50°; at higher temperatures complex condensation products result.

5. The length of time required for the hydrogenation varies with the size of the run and the activity of the catalyst. For a 9-mole run the hydrogenation usually proceeds for 10–12 hours before external heating is needed to bring the temperature into the 45–50° range. The system is periodically recharged with hydrogen to maintain a pressure of about 1800 lb. Reduction is continued until a total of 9.0 moles of hydrogen has been absorbed. Absorption of the calculated amount of hydrogen serves as the criterion for stopping the hydrogenation. For the 2.0-mole run described, 4–5 hours are needed.

6. The conversion of resorcinol to 2-methyl-1,3-cyclohexanedione can be effected by first isolating the dihydroresorcinol² and subjecting it to the methylation reaction. However, this procedure is more laborious and the yield is no better.

7. The checkers found that filtration through a coarse sintered-glass funnel is rapid and better-quality product is obtained. When a medium-porosity sintered-glass funnel or Büchner funnel is used, the filtration is exceedingly slow and may even stop owing to a small amount of gelatinous impurity which is present.

8. If all the sodium iodide is not removed by the washings with water, the product tends to become yellow.

9. This product is sufficiently pure for use in conversion to 1,6-dioxo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene.^{3,4}

3. Discussion

2-Methyl-1,3-cyclohexanedione has been prepared by cyclization of ethyl 5-oxoheptanoate⁵ and methyl 5-oxoheptanoate³ with sodium ethoxide and sodium methoxide, respectively, and by methylation of dihydroresorcinol² employing sodium methoxide in methanol,^{3,6} potassium hydroxide in aqueous methanol,⁷ potassium methoxide in methanol,⁸ potassium hydroxide in aqueous acetone,⁹ potassium carbonate in aqueous acetone,⁴ or sodium ethoxide in ethanol.¹⁰ The present method is essentially that of Stetter,⁷ except that the unnecessary isolation of the intermediary dihydroresorcinol is omitted, and this greatly enhances the ease of preparation.

4. Merits of Preparation

2-Methyl-1,3-cyclohexanedione has been used as starting material for the syntheses of several polycyclic compounds for projected syntheses of steroids and terpenoids.^{11,12,13} It has also been used to prepare 1,6-diketo-8a-methyl-1,2,3,4,6,7,8,8a-octahydronaphthalene.^{3,4,14,15}

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 5*, 486
- *Org. Syn. Coll. Vol. 7*, 368
- *Org. Syn. Coll. Vol. 8*, 312

References and Notes

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

ethanol (64-17-5)

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

methanol (67-56-1)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

aluminum (7429-90-5)

nickel,
Raney nickel (7440-02-0)

acetone (67-64-1)

sodium methoxide (124-41-4)

potassium hydroxide (1310-58-3)

sodium ethoxide (141-52-6)

Methyl iodide (74-88-4)

sodium iodide (7681-82-5)

resorcinol (108-46-3)

dioxane (123-91-1)

potassium methoxide (865-33-8)

Dihydroresorcinol

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

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

ethyl 5-oxoheptanoate

methyl 5-oxoheptanoate