



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.

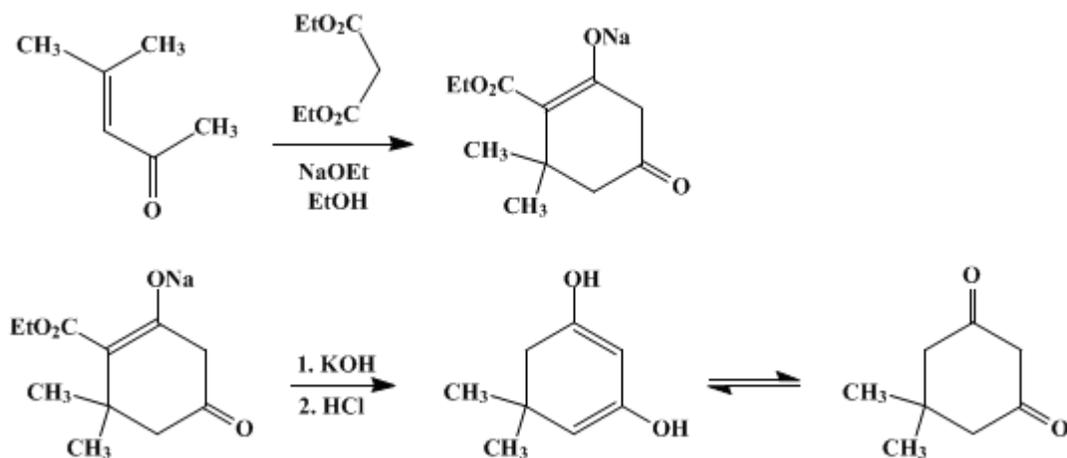
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.200 (1943); Vol. 15, p.14 (1935).

5,5-DIMETHYL-1,3-CYCLOHEXANEDIONE

[1,3-Cyclohexanedione, 5,5-dimethyl-]



Submitted by R. L. Shriner and H. R. Todd.
Checked by W. H. Carothers and W. L. McEwen.

1. Procedure

In a dry 2-l. three-necked, round-bottomed flask, fitted with a liquid-sealed stirrer, a 500-cc. dropping funnel, and an efficient reflux condenser protected at the top with a calcium chloride tube, is placed 400 cc. of absolute alcohol. Through the condenser tube is added 23 g. (1 gram atom) of clean sodium at such a rate that the solution is kept at the boiling temperature. After the sodium has dissolved completely, 170 g. (1.06 moles) of ethyl malonate is added, and then 100 g. (1.02 moles) of mesityl oxide (Note 1) is added slowly through the dropping funnel. The solution is refluxed with constant stirring for two hours, after which a solution of 125 g. (2.2 moles) of potassium hydroxide in 575 cc. of water is added and the mixture is stirred and refluxed again on the water bath for six hours.

The mixture while still hot is made just acid to litmus with dilute hydrochloric acid (1 volume concentrated acid to 2 volumes water; sp. gr. 1.055); about 550 cc. is required. The flask is fitted with a condenser set for distillation, and as much alcohol as possible (about 550 cc.) is distilled by heating on a water bath.

The residue in the flask is boiled with about 15 g. of Norite (Note 2), filtered, and the treatment with the decolorizing charcoal repeated. The residue is again neutralized to litmus with dilute hydrochloric acid (about 150 cc.) and again boiled with charcoal. The hot, neutral or alkaline, yellow filtrate is finally made distinctly acid to methyl orange with additional dilute hydrochloric acid (50 to 100 cc.), boiled for a few minutes, and allowed to cool, whereupon the methone crystallizes. The product is filtered by suction from the acid liquid, washed with ice-cold water, and dried in the air. The yield is 96–122 g. (67–85 per cent of the theoretical amount) (Note 3).

2. Notes

1. The yield of methone depends on the purity of the mesityl oxide (*Org. Syn. Coll. Vol. I, 1941, 345*), which should be freshly distilled, the fraction boiling at 126–131° being collected.
2. Care is necessary when adding the decolorizing charcoal or the hot acid solution may foam vigorously owing to the liberation of carbon dioxide. A large container should be used, and the charcoal should be added very slowly.
3. The submitters in carrying out this preparation invariably obtained yields ranging from 120 to 128 g. of a product melting between 145° and 147°. Crystallization from about 1 l. of acetone gave 100 g. (70

per cent) of pure white material melting at 147°. The checkers (using [mesityl oxide](#) purchased from the Eastman Kodak Co. and freshly distilled) obtained yields ranging from 96 to 112 g., but their product melted at 147–148° and recrystallization failed to raise the melting point. The melting point of methone is given in the literature as 148–150°.

3. Discussion

[5,5-Dimethyldihydroresorcinol](#), [methone](#), [dimedone](#), has always been made from [mesityl oxide](#) and malonic ester. The procedure given above is that of Vorländer.¹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 345](#)

References and Notes

1. Vorländer and Erig, *Ann.* **294**, 314 (1897); Vorländer, *Z. anal. Chem.* **77**, 245 (1929); *Z. angew. Chem.* **42**, 46 (1929); Chavanne, Miller, and Cornet, *Bull. soc. chim. Belg.* **40**, 673 (1931).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[alcohol](#) (64-17-5)

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

[carbon dioxide](#) (124-38-9)

[acetone](#) (67-64-1)

[Norite](#) (7782-42-5)

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

[sodium](#) (13966-32-0)

[Mesityl oxide](#) (141-79-7)

[ethyl malonate](#) (1071-46-1)

[5,5-Dimethyl-1,3-cyclohexanedione](#),
[1,3-Cyclohexanedione, 5,5-dimethyl-](#),
[methone](#),
[dimedone](#) (126-81-8)

[5,5-Dimethyldihydroresorcinol](#)

[methyl orange](#) (547-58-0)

