Organic Syntheses

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.

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.

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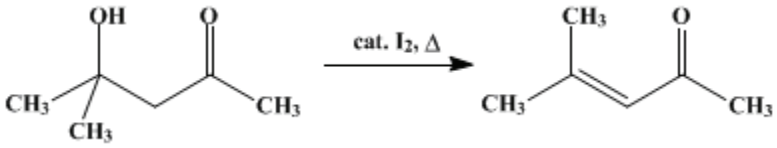
MESITYL OXIDE



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1. Procedure

A 1-l. round-bottomed flask is fitted with a three-bulbed Glinsky fractionating column connected to a water-cooled condenser set for distillation. The crude diacetone alcohol (p. 199) which will usually weigh about 1100 g. (9.5 moles) and will have a specific gravity of about 0.91 is placed in the flask together with 0.1 g. of iodine. The mixture is now distilled steadily but not too rapidly (Note 1) with a small free flame, and three portions are collected as follows: I, 56–80°; II, 80–126°; III, 126–131° (Note 2). The first portion is acetone containing a small amount of mesityl oxide and water (Note 3). The second portion separates into two layers—water and crude mesityl oxide. The third portion is pure mesityl oxide.

While the third fraction is distilling, the aqueous layer in fraction II is separated in a separatory funnel and the crude mesityl oxide is dried with anhydrous calcium chloride and distilled through a Glinsky column; by this means a further amount of acetone and a small intermediate fraction (85-126°), which is best discarded, are separated. The pure mesityl oxide itself then distils between 126° and 130° and is added to the pure product already obtained as the third portion of the first distillation. The first complete distillation will require about five hours; the redistillation of portion III will take about one hour. The yield is 650 g. (65 per cent of the theoretical amount based on the total acetone employed) (Note 4). About 300 g. of acetone is recovered (Note 3).

2. Notes

1. The first distillation should not be interrupted but should be carried out at a slow uniform rate until complete.
2. The very last portion of fraction III is sometimes slightly colored, apparently by some iodine which comes over at the end of the distillation. A small amount of high-boiling residue is always left.
3. The acetone recovered from the preparation of mesityl oxide can be mixed with fresh acetone and used successfully in preparing more crude diacetone alcohol (p. 199).
4. If the crude diacetone alcohol contains less than 80 per cent of diacetone alcohol (when the refluxing is not carried out long enough, for example) the yield of mesityl oxide will be, of course, correspondingly low.

3. Discussion

There are two general methods for the preparation of mesityl oxide: the action of condensing agents (hydrochloric acid, etc.) on acetone, [1] and the dehydration of diacetone alcohol. [2] The action of acid condensing agents is very unsatisfactory; the yields are poor and considerable quantities of phorone and similar substances are invariably produced. The direct production of mesityl oxide from acetone and calcium oxide[3] was tried, but without success; diacetone alcohol was the principal product. Several methods proposed for the dehydration of diacetone alcohol were investigated. That of Hibbert[2] (using a very small quantity of iodine) is superior to the action of either concentrated sulfuric acid or aluminum phosphate.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 196
- Org. Syn. Coll. Vol. 2, 200

References and Notes

1. Fitting, Ann. **110**, 32 (1859); Heintz, Ann. **178**, 343 (1875); Claisen, Ann. **180**, 4 (1875); Freer and Lachmann, Am. Chem. J. **19**, 887 (1897); Currie, J. Am. Chem. Soc. **35**, 1061 (1913); Couturier and Meunier, Compt. rend. **140**, 721 (1905); Mannich and Hâncu, Ber. **41**, 574 (1908); Bodroux and Taboury, Bull. soc. chim. (4) **3**, 829 (1908); Yllner, Svensk. Kem. Tids. **37**, 227 (1925) [C. A. **20**, 739 (1926)]; Gasopoulos, Ber. **59**, 2188 (1926); Brederick, Lehmann, Schönfeld, and Fritsche, Ber. **72**, 1417 (1939).
2. Heintz, Ann. **178**, 351 (1875); Kohn, Monatsh. **34**, 779 (1913), Ger. pat. 208,635 [Frdl. **9**, 62 (1908–10)]; Kyriakides, J. Am. Chem. Soc. **36**, 534 (1914); Hibbert, ibid. **37**, 1748 (1915); Hoffman, U. S. pat. 1,474,035 [C. A. **18**, 401 (1924)]; Locquin, Ann. chim. (9) **19**, 32 (1923).
3. Hoffman, J. Am. Chem. Soc. **31**, 722 (1909); Hertkorn, Ger. pat. 258,057 [Frdl. **11**, 46 (1912–14)].

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

Diacetone alcohol

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

iodine (7553-56-2)

acetone (67-64-1)

Mesityl oxide (141-79-7)

calcium oxide

aluminum phosphate (7784-30-7)