



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.

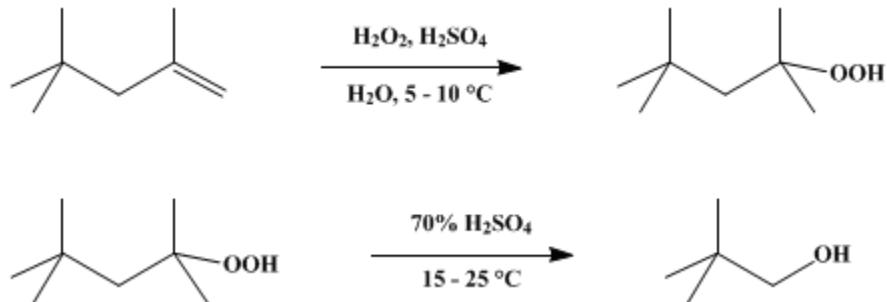
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

Organic Syntheses, Coll. Vol. 5, p.818 (1973); Vol. 40, p.76 (1960).

NEOPENTYL ALCOHOL

[2,2-Dimethyl-1-propanol]



Submitted by Joseph Hoffman¹

Checked by John D. Roberts and J. Eric Nordlander.

1. Procedure

A. Preparation of *hydroperoxide*. In a 2-l. three-necked round-bottomed flask, equipped with a mechanical stirrer (Note 1), a dropping funnel, and a thermometer, is placed 800 g. of 30% *hydrogen peroxide* (Note 2). The flask is surrounded by an ice bath and rapid stirring is started. In the meantime, 800 g. of 95–96% *sulfuric acid* is added to 310 g. of cracked ice and the solution is cooled to 10°. When the temperature of the *hydrogen peroxide* reaches 5–10°, the cold *sulfuric acid* is added slowly from the dropping funnel during a period of about 20 minutes (Note 3). The temperature of the solution should not exceed 20° during the addition. Commercial diisobutylene (224.4 g., 2 moles) is now added over a period of 5–10 minutes. The ice bath is removed and replaced by a water bath maintained at approximately 25° (Note 4). Vigorous agitation is maintained for 24 hours (Note 5). At the end of this time, mixing is discontinued, the mixture is transferred to a 2-l. separatory funnel and the two layers are allowed to separate (Note 6).

B. Decomposition of *hydroperoxide*. The upper organic layer (240–250 g.) is removed (Note 7) and added with vigorous stirring to 500 g. of 70% *sulfuric acid* in a 1-l. three-necked round-bottomed flask fitted with thermometer, stirrer, and dropping funnel and surrounded by an ice bath. The reaction temperature is maintained at 15–25° during addition, which requires 65–75 minutes (Note 8). Stirring is continued for 30 minutes at 5–10°, and then the reaction mixture is allowed to stand (0.5–3 hours) until the two layers are completely separated. The mixture is now transferred to a 1-l. separatory funnel and allowed to stand for about 15 minutes, after which time the lower layer is drawn off into 1 l. of water. The resulting mixture is distilled from a 3-l. flask without fractionation. The distillation is complete when 50–100 ml. of water has been collected (Note 9). The upper organic layer from the distillate (180–190 g.) is removed and dried over anhydrous *magnesium sulfate* (Note 10). The dried organic layer is filtered with the aid of a small amount of *ether* and distilled through an efficient fractionating column. The fraction which boils at 111–113° is collected (Note 11) and (Note 12). The yield is 60–70 g. (34–40% of theory, based upon the diisobutylene).

2. Notes

1. A heavy nichrome wire twisted into 4 loops (similar to an egg beater) was found to be very satisfactory. The two ends of the wire, extending several inches beyond the loops, were pushed into a piece of glass tubing for the stirrer shaft.
2. If the *hydrogen peroxide* is slightly below 30%, enough should be used to give the amount called for. The acid concentration should be maintained by increasing the *sulfuric acid* proportionately.
3. The *hydrogen peroxide-sulfuric acid* solution consists of approximately 12.5% *hydrogen peroxide* and 40% *sulfuric acid*.

4. Good results have been obtained in the temperature range 23–27°. Although the heat given off during the reaction is not great and is spread over a long period of time, the reaction vessel must nevertheless be surrounded by a water bath. If the room temperature is in the range indicated, no further regulation of the water bath temperature is required.

5. It is necessary to provide rapid and vigorous stirring in order to obtain good results.

6. The aqueous layer now contains approximately 8% **hydrogen peroxide**. This layer may be reused by adjusting the **hydrogen peroxide** percentage to 12.5 by use of either 30% or 50% **hydrogen peroxide**. The **sulfuric acid** must be readjusted to 40%. Approximately 1.9 kg. of aqueous layer is required for 2 moles of diisobutylene.

7. The submitter states that the procedure may be interrupted at this point by washing the organic layer free of acid with a saturated solution of **sodium bicarbonate** and that the **hydroperoxide** concentrate will keep for a long time, especially if refrigerated.

8. Care should be taken in decomposing the **hydroperoxide**. If the temperature is kept too low, decomposition takes place too slowly and **hydroperoxide** may accumulate. Heat is liberated during the decomposition, and after each small addition the temperature will rise. At the start, small amounts of **hydroperoxide** are added until the temperature rises above 15°; the rate is then adjusted to keep the temperature in the range 15–25°. The rise in temperature after each small addition is the best evidence that decomposition is actually taking place.

9. The submitter states that, when the distillation is essentially complete, there is a tendency for the residue to foam; this should be watched for and the heat should be turned back to avoid carryover into the distillate. The checkers did not experience any difficulties of this sort.

10. The checkers found that the commercial grade of "dried" **magnesium sulfate** was not completely effective and, even after three treatments with fresh drying agent, the subsequent distillation afforded an azeotrope of **neopentyl alcohol** and water of b.p. 80–85°. The organic layer of the azeotrope had to be separated from the water, dried, and redistilled to give the stated total yields.

11. The fraction between 95° and 110° should be taken off at a high reflux ratio; toward the end of the distillation the reflux ratio should again be increased. Most of the product comes over at 113°.

12. Pure **neopentyl alcohol** melts at about 55°. From time to time it will be necessary to circulate hot water through the take-off condenser in order to facilitate removal of the alcohol.

3. Discussion

Neopentyl alcohol has been made by **lithium aluminum hydride** reduction of **trimethylacetic acid**² and by treating **tert-butyldimagnesium chloride** with **methyl formate**.³

The preparation of **neopentyl alcohol** from diisobutylene herein described represents an example of acid-catalyzed addition of **hydrogen peroxide** to a branched olefin, followed by an acid-catalyzed rearrangement of the tertiary **hydroperoxide** formed. In addition to **neopentyl alcohol**, there are formed **acetone** and also small amounts of **methanol** and **methyl neopentyl ketone** by an alternative rearrangement of the **hydroperoxide**.

References and Notes

1. Air Reduction Co., Murray Hill, New Jersey.
2. R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).
3. L. H. Sommer, H. D. Blankman, and P. C. Miller, *J. Am. Chem. Soc.*, **76**, 803 (1954).

Appendix

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

diisobutylene

sulfuric acid (7664-93-9)

methanol (67-56-1)

ether (60-29-7)

sodium bicarbonate (144-55-8)

acetone (67-64-1)

hydrogen peroxide (7722-84-1)

methyl formate (107-31-3)

Trimethylacetic acid (75-98-9)

magnesium sulfate (7487-88-9)

lithium aluminum hydride (16853-85-3)

hydroperoxide

2,2-Dimethyl-1-propanol,
Neopentyl alcohol (75-84-3)

hydrogen peroxide-sulfuric acid

methyl neopentyl ketone (590-50-1)

tert-butylmagnesium chloride (677-22-5)