



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.

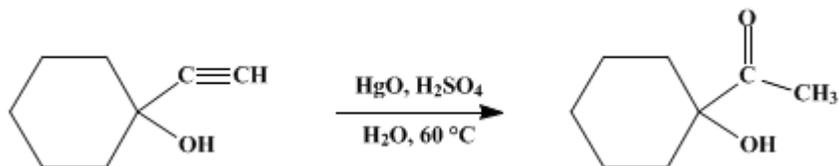
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## 1-ACETYLCYCLOHEXANOL

[Ketone, 1-hydroxycyclohexyl methyl]



Submitted by Gardner W. Stacy and Richard A. Mikulec<sup>1</sup>.

Checked by John C. Sheehan, George A. Mortimer, and Norman A. Nelson.

### 1. Procedure

In a 1-l. three-necked round-bottomed flask, equipped with a sealed stirrer, a reflux condenser, a thermometer, and a dropping funnel, is dissolved 5 g. of mercuric oxide (Note 1) in a solution of 8 ml. of concentrated sulfuric acid and 190 ml. of water. The solution is warmed to 60°, and 49.7 g. (0.40 mole) of 1-ethynylcyclohexanol (Note 2) is added dropwise over a period of 1.5 hours. After the addition has been completed, the reaction mixture is stirred at 60° for an additional 10 minutes and allowed to cool. The green organic layer which settles is taken up in 150 ml. of ether, and the aqueous layer is extracted with four 50-ml. portions of ether (Note 3). The combined ethereal extracts are washed with 100 ml. of saturated sodium chloride solution (Note 4) and dried over anhydrous sodium sulfate. The drying agent is removed, the ether is evaporated, and the residue is distilled under reduced pressure through a 15-cm. column packed with glass helices. The 1-acetylcyclohexanol is collected at 92–94°/15 mm. as a colorless liquid,  $n_D^{25}$  1.4670,  $d_4^{25}$  1.0248 (Note 5). The yield is 37–38 g. (65–67%).

### 2. Notes

1. Mallinckrodt mercuric oxide red (analytical reagent or N.F. 1x grade) was used.
2. 1-Ethynylcyclohexanol is available commercially. It may be prepared as reported by Saunders.<sup>2</sup>
3. To facilitate subsequent extractions, the solid material remaining after separation of as much of the aqueous phase as possible should be removed by gentle suction filtration and washed with 25 ml. of ether.
4. The sodium chloride solution removes the green color from the ether extract, leaving a yellow solution.
5. The checkers found b.p. 100°/21 mm.,  $n_D^{25}$  1.4662–1.4665,  $d_4^{25}$  1.0235–1.0238. Others have reported b.p. 92–94°/12 mm.,  $d_0^{20}$  1.0256;<sup>3</sup> b.p. 91°/11 mm.,  $n_D^{11}$  1.4726,  $d_4^{11}$  1.1033;<sup>4</sup> b.p. 88.0–88.6°/12 mm.,  $n_D^{28}$  1.4712.<sup>5</sup>

Establishing a criterion for the purity of the product is of particular importance because of the known tendency of ethynylcarbinols to undergo rearrangement.<sup>5,6</sup> The authors have reported that consecutive small fractions of the distillate possess a constant boiling point and refractive index. Furthermore, representative fractions, treated with periodic acid and subsequently with 2,4-dinitrophenylhydrazine, give cyclohexanone 2,4-dinitrophenylhydrazone in 83% over-all yield in a high state of purity.

### 3. Discussion

1-Acetylcyclohexanol has been prepared by the hydrolysis of 1-bromo-1-acetylcyclohexane<sup>3</sup> and of 1-acetoxy-1-acetylcyclohexane oxime,<sup>7</sup> by the hydration of 1-ethynylcyclohexanol,<sup>4,5,8,9,10,11,12</sup> by the treatment of 1-hydroxycyclohexanecarboxylic acid with methyl lithium<sup>13,14</sup> and by the hydrolysis of 1-(isopropoxyethoxy)-1-(1-iminoethyl)cyclohexane.<sup>15</sup> and 1-(2-tetrahydropyranoxy)-1-(1-iminoethyl)cyclohexane.<sup>16</sup> The present procedure is based upon that of Stacy and Mikulec for the preparation of 1-acetylcyclopentanol.<sup>6</sup>

## References and Notes

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

sulfuric acid (7664-93-9)

ether (60-29-7)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

mercuric oxide (21908-53-2)

2,4-Dinitrophenylhydrazine (119-26-6)

1-Ethynylcyclohexanol (78-27-3)

1-Acetylcyclohexanol,  
Ketone, 1-hydroxycyclohexyl methyl (1123-27-9)

periodic acid

cyclohexanone 2,4-dinitrophenylhydrazone (1589-62-4)

1-bromo-1-acetylcyclohexane

1-acetoxy-1-acetylcyclohexane oxime

1-hydroxycyclohexanecarboxylic acid

Methylithium (917-54-4)

1-(isopropoxyethoxy)-1-(1-iminoethyl)cyclohexane

1-(2-tetrahydropyranoxy)-1-(1-iminoethyl)cyclohexane

1-acetylcyclopentanol