



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.

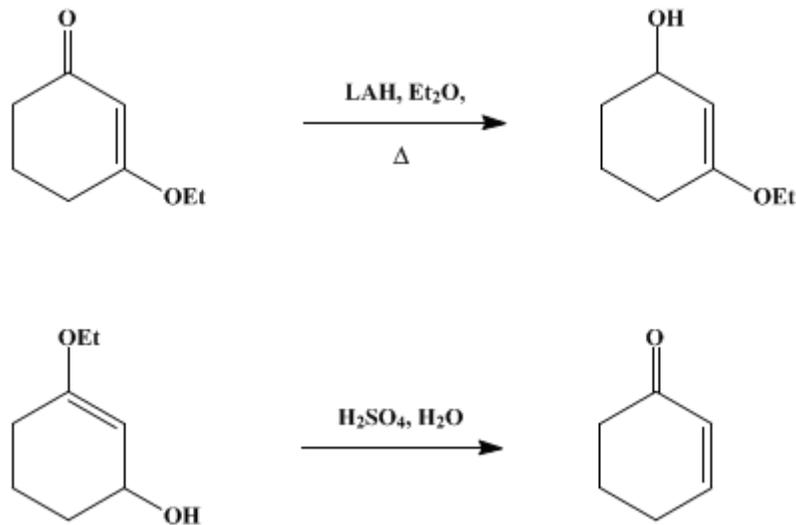
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.294 (1973); Vol. 40, p.14 (1960).*

## 2-CYCLOHEXENONE



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### 1. Procedure

In a dry 500-ml. three-necked flask, equipped with a reflux condenser, a mechanical stirrer, and a dropping funnel and protected from atmospheric moisture with drying tubes, are placed 6.0 g. (0.16 mole) of lithium aluminum hydride and 200 ml. of anhydrous ether. A solution of 43 g. (0.307 mole) of 3-ethoxy-2-cyclohexenone (Note 1) in 50 ml. of anhydrous ether is added, dropwise and with stirring, to the reaction flask at a rate which maintains gentle refluxing of the solvent (Note 2). After the addition is complete, the reaction solution is boiled under reflux for an additional 30 minutes and then allowed to cool. The complex is hydrolyzed and the excess lithium aluminum hydride is destroyed by the cautious addition, dropwise and with stirring, of 15 ml. of water (Note 3). The resulting reaction mixture is poured into 500 ml. of cold aqueous 10% sulfuric acid. The ether layer which forms is separated, and the residual aqueous phase is extracted with three 300-ml. portions of ether. The combined ether solutions are washed successively with one 100-ml. portion of water and one 100-ml. portion of saturated, aqueous sodium bicarbonate solution and then dried over magnesium sulfate. The ether is removed by distillation through a 50-cm. Vigreux column, and the residue is distilled under reduced pressure through a 40-cm. spinning-band column (Note 4). The yield of 2-cyclohexenone (Note 5), b.p. 56–57.5°/10 mm. or 96–97°/72 mm.,  $n_D^{27}$  1.4858, is 18.2–22.1 g. (62–75%).

### 2. Notes

1. The preparation of 3-ethoxy-2-cyclohexenone is described elsewhere in this volume.<sup>2</sup> (It has been reported that 3-isobutoxy-2-cyclohexenone can be prepared in somewhat higher yield than the 3-ethoxy compound by the same procedure and that the 3-isobutoxy compound is just as useful for the present preparation (private communication from D. A. H. Taylor).
2. This addition requires approximately 1.5 hours.
3. The addition of water is accompanied by foaming, and care must be taken to avoid excessive loss of the solvent.
4. The 2-cyclohexenone obtained by an ordinary distillation at this point is contaminated with lower-boiling impurities (see (Note 5)), primarily ether and ethanol.
5. The purity of the 2-cyclohexenone may be assayed by gas chromatography on an 8 mm. × 215 cm. column heated to 125° and packed with di-(2-ethylhexyl) sebacate suspended on ground firebrick. This method of analysis indicates that the 3-cyclohexenone in the product amounts to no more than 3%. The

fore-run from this fractional distillation contains substantial amounts of 2-cyclohexenone accompanied by ether, ethanol, and minor amounts of other lower-boiling impurities. Additional quantities of pure 2-cyclohexenone can be recovered by redistillation of this fore-run. The preparation of 2-cyclohexenone has been run on twice the scale described with no loss in yield. The ultraviolet spectrum of an ethanol solution of the 2-cyclohexenone obtained has a maximum at 226 m $\mu$  ( $\epsilon = 10,400$ ).

### 3. Discussion

2-Cyclohexenone has been prepared by dehydrohalogenation of 2-bromocyclohexanone,<sup>3,4</sup> by the hydrolysis and oxidation of 3-chlorocyclohexene,<sup>5</sup> by the dehydration of  $\alpha$ -hydroxycyclohexanone,<sup>6</sup> by the oxidation of cyclohexene with chromic acid<sup>7</sup> or hydrogen peroxide in the presence of a vanadium catalyst,<sup>8</sup> by the addition of acrolein to ethyl acetoacetate followed by cyclization, hydrolysis, and decarboxylation,<sup>9</sup> by the reduction of N,N-dimethylaniline with sodium and ethanol in liquid ammonia followed by hydrolysis,<sup>10</sup> by the reduction of anisole with lithium in liquid ammonia,<sup>11</sup> and by the reduction of 3-alkoxy-2-cyclohexanones with lithium aluminum hydride followed by acid-catalyzed hydrolysis and rearrangement.<sup>12</sup>

The procedure described illustrates a general method for the preparation of  $\alpha,\beta$ -unsaturated aldehydes and ketones from the enol ethers of  $\beta$ -dicarbonyl compounds.<sup>12,13,14</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 539
- Org. Syn. Coll. Vol. 6, 679

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### References and Notes

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### Appendix

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

ethanol (64-17-5)

sulfuric acid (7664-93-9)

ammonia (7664-41-7)  
ether (60-29-7)  
Acrolein (107-02-8)  
sodium bicarbonate (144-55-8)  
Cyclohexene (110-83-8)  
Anisole (100-66-3)  
sodium (13966-32-0)  
chromic acid (7738-94-5)  
hydrogen peroxide (7722-84-1)  
N,N-dimethylaniline (121-69-7)  
Ethyl acetoacetate (141-97-9)  
lithium (7439-93-2)  
magnesium sulfate (7487-88-9)  
Vanadium (7440-62-2)  
lithium aluminum hydride (16853-85-3)  
2-bromocyclohexanone  
 $\alpha$ -hydroxycyclohexanone  
2-Cyclohexenone (930-68-7)  
3-Ethoxy-2-cyclohexenone (5323-87-5)  
3-isobutoxy-2-cyclohexenone  
3-cyclohexenone  
3-chlorocyclohexene