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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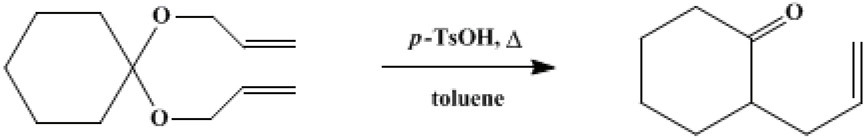
2-ALLYLCYCLOHEXANONE

[Cyclohexanone, 2-allyl-]



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1. Procedure

A solution of 196 g. (1 mole) of cyclohexanone diallyl acetal (Note 1), 150 g. of toluene, and 0.10 g. of *p*-toluenesulfonic acid is distilled through a good fractionating column (Note 2). In about 3 hours, 110 g. of distillate boiling at 91–92° (Note 3) is obtained and the temperature in the head then rises abruptly. The residue in the distilling flask is cooled and washed with 5 ml. of aqueous potassium carbonate to remove the acid. The remaining solution is passed through a filter containing anhydrous powdered magnesium sulfate and returned to the still. Most of the remaining toluene is removed by distillation at 100 mm. pressure (b.p. 52°). The receiver is changed, the pressure is reduced to 15 mm., and the last of the toluene is collected in a cold trap. The residual oil is rapidly vacuum-distilled to separate the product from a higher-boiling residue. Redistillation yields 117–126 g. (85–91%) of 2-allylcyclohexanone, b.p. 86–88°/15 mm., n_{D}^{25} 1.4670.

2. Notes

1. The preparation of cyclohexanone diallyl acetal is described on p. 292.
2. A 14-in. helices-packed column is sufficient.
3. This distillate is the azeotrope of toluene and allyl alcohol whose composition is about 50% allyl alcohol by weight.[2]

3. Discussion

2-Allylcyclohexanone has been prepared from the sodium derivative of cyclohexanone by alkylation with allyl bromide[3] or with allyl iodide,[4] and by ketonic hydrolysis of ethyl 1-allyl-2-ketocyclohexanecarboxylate.[5,6]

4. Merits of Preparation

This procedure, when combined with the preparation of allyl ketals (p. 292), provides a general method for obtaining allyl substitution alpha to a carbonyl group. A discussion of some of these applications, as well as the vinyl allyl ether rearrangement which is involved, has been given by Hurd and Pollack.[7] Also, the procedure can be repeated to allow the introduction of more than one allyl group.

References and Notes

1. The Dow Chemical Company, Texas Division, Freeport, Texas.
2. L. H. Horsley and co-workers, *Advances in Chem. Ser.*, No. 6, Azeotropic Data, American Chemical Society, Washington, 1955, p. 83.
3. C. A. VanderWerf and L. V. Lemmerman, *Org. Syntheses* Coll. Vol. 3, 44 (1955).
4. R. Cornubert, *Ann. Chim.*, [9] **16, 145** (1921).
5. A. C. Cope, K. E. Hoyle, and D. Heyl, *J. Am. Chem. Soc.*, **63**, 1848 (1941).
6. R. Grëwe, *Ber.*, **76**, 1075 (1943).

7. C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1905 (1938).

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

sodium derivative of cyclohexanone

potassium carbonate (584-08-7)

Allyl bromide (106-95-6)

Allyl alcohol (107-18-6)

allyl iodide (556-56-9)

toluene (108-88-3)

magnesium sulfate (7487-88-9)

2-Allylcyclohexanone,
Cyclohexanone, 2-allyl- (94-66-6)

ethyl 1-allyl-2-ketocyclohexanecarboxylate

Cyclohexanone diallyl acetal (53608-84-7)

p-toluenesulfonic acid (104-15-4)