



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.

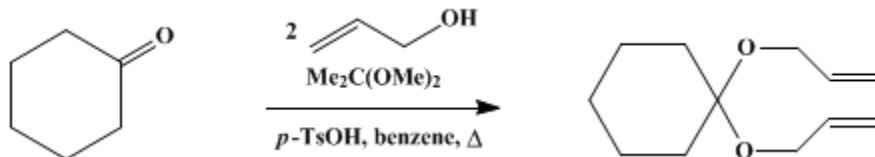
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.292 (1973); Vol. 42, p.34 (1962).

CYCLOHEXANONE DIALLYL ACETAL



Submitted by W. L. Howard and N. B. Lorette¹.
Checked by E. J. Corey and R. A. E. Winter.

1. Procedure

A solution of 294 g. (3 moles) of [cyclohexanone](#), 343 g. (3.3 moles) of [acetone dimethyl acetal](#), 418 g. (7.2 moles) of [allyl alcohol](#), 1 l. of [benzene](#), and 0.2 g. of [p-toluenesulfonic acid monohydrate](#) ([Note 1](#)) is distilled using a good fractionating column until the [acetone](#) and the benzene-methanol azeotrope are completely removed ([Note 2](#)). The solution is cooled below the boiling point, and a solution of 0.5 g. of [sodium methoxide](#) in 20 ml. of [methanol](#) is added all at once with stirring ([Note 3](#)). Distillation is resumed, and unreacted [allyl alcohol](#) and [benzene](#) are removed at atmospheric pressure and then at reduced pressure ([Note 4](#)). Distillation is continued at a pressure in the range 5–20 mm. to remove forerun (on the order of 100 ml.) ([Note 5](#)). The [cyclohexanone diallyl acetal](#), b.p. 84°/5 mm., 98°/10 mm., 114°/20 mm., n_D^{25} 1.4600, is then collected. The yield is 382–435 g. (65–74%). A small amount of higher-boiling residue remains.

2. Notes

- Commercial [acetone dimethyl acetal](#) and [allyl alcohol](#) from The Dow Chemical Company and [cyclohexanone](#) from Eastman Kodak Company were used without further treatment.
- These reaction products distil within a narrow range. The head temperature was maintained in the range 56–59°. About 750 ml. of distillate is collected, depending on the efficiency of fractionation. The combined amount of [methanol](#) and [acetone](#) may be estimated by washing an aliquot of the distillate with 2 volumes of water and taking the difference between the original volume and that of the residual [benzene](#) as the volume of [methanol-acetone](#). Usually this is about 450 ml. The distillation should be as rapid as possible to avoid the formation of by-product [2-allylcyclohexanone](#). A 1.9 × 120 cm. vacuum-jacketed, silvered column packed with 0.25-in. glass helices and fitted with a vapor-dividing head controlled by a timed relay was used. The checkers used a 1.3 × 92 cm. vacuum-jacketed, silvered column packed with 0.25-in. glass ring chains. With this column it was necessary to carry out the distillation of [benzene-acetone-methanol](#) using reflux ratios varying from 2:1 initially to 11:1 at the conclusion. The use of a shorter column is not satisfactory.
- Other soluble, non-volatile bases may be used to neutralize the acid. The reactants may be kept at room temperature safely after addition of base.
- An azeotrope of [benzene](#) and [allyl alcohol](#) distils at about 77°, followed by [benzene](#). When the temperature in the boiling flask reaches 120–130°, the pressure is reduced and the remaining [benzene](#) is taken to a cold trap.
- The forerun contains some [acetone diallyl acetal](#) and about 35–40 g. of [2-allylcyclohexanone](#), b.p. 78°/10 mm.

3. Discussion

[Cyclohexanone diallyl acetal](#) has been prepared from [cyclohexanone](#) and [allyl orthosilicate](#)² and by the above procedure.³

4. Merits of Preparation

The preparation given here is operable for a large number of ketone acetals, including those formed from both primary and secondary alcohols and from alcohols and ketones containing other functional groups which are stable under the conditions used.³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 25](#)
- [Org. Syn. Coll. Vol. 8, 578](#)

References and Notes

1. The Dow Chemical Company, Texas Division, Freeport, Texas.
 2. B. Helferich and J. Hausen, *Ber.*, **57B**, 795 (1924) [*C.A.*, **18**, 2869 (1924)].
 3. N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960).
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Appendix

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

benzene-methanol azeotrope

[Benzene \(71-43-2\)](#)

[methanol \(67-56-1\)](#)

[Cyclohexanone \(108-94-1\)](#)

[Allyl alcohol \(107-18-6\)](#)

[acetone \(67-64-1\)](#)

[sodium methoxide \(124-41-4\)](#)

[2-Allylcyclohexanone \(94-66-6\)](#)

[methanol-acetone \(590-90-9\)](#)

[acetone dimethyl acetal \(77-76-9\)](#)

[Cyclohexanone diallyl acetal \(53608-84-7\)](#)

[benzene-acetone-methanol](#)

[acetone diallyl acetal](#)

[allyl orthosilicate](#)

[p-toluenesulfonic acid monohydrate \(6192-52-5\)](#)

