



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.

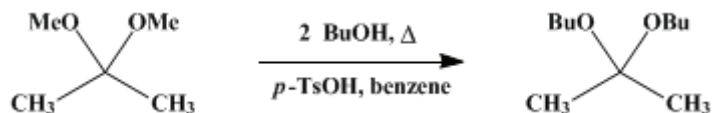
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.5 (1973); Vol. 42, p.1 (1962).

ACETONE DIBUTYL ACETAL

[Propane, 2,2-dibutoxy-]



Submitted by N. B. Lorette and W. L. Howard¹.

Checked by Max Tishler and Stanley Nusim..

1. Procedure

A mixture of 312 g. (3 moles) of [acetone dimethyl acetal](#) ([Note 1](#)), 489 g. (6.6 moles) of [butanol](#), 1.0 l. of [benzene](#), and 0.2 g. of [p-toluenesulfonic acid](#) is placed in a 3-l. flask. The flask is connected to a packed fractionating column and the solution distilled until the azeotrope of [benzene](#) and [methanol](#), boiling at 58°, is completely removed ([Note 2](#)). The contents of the boiler are then cooled below the boiling point and a solution of 0.5 g. of [sodium methoxide](#) in 20 ml. of [methanol](#) ([Note 3](#)) is added all at once with stirring. The flask is replaced for further distillation, and most of the remaining [benzene](#) is distilled at atmospheric pressure. The pressure is then reduced, and the remaining [benzene](#) and unreacted [butanol](#) are removed ([Note 4](#)). Finally, the pressure is reduced to 20 mm., the last traces of low-boiling materials are taken to the cold trap, and the product is distilled. After a small fore-run, [acetone dibutyl acetal](#) is collected at 88–90°/20 mm. The yield is 421–453 g. (74.6–80.3%), n_D^{25} 1.4105, d_4^{25} 0.8315.

2. Notes

1. Commercial [acetone dimethyl acetal](#) (2,2-dimethoxypropane) from the Dow Chemical Company was used without further treatment.

2. About 570 ml. of this azeotrope is obtained. The [methanol](#) produced may be estimated by washing an aliquot with about two volumes of water in a graduated cylinder. The [methanol](#) content is approximately the difference between the initial volume and that of the residual [benzene](#) phase, and about 230 ml. is obtained, depending on the efficiency of fractionation. Other hydrocarbons, e.g., [hexane](#) or [cyclohexane](#), can be used for the removal of [methanol](#).

The submitters' distillation was carried out in a 19 × 1200-mm. vacuum-jacketed silvered column fitted with a magnetically operated vapor-takeoff head controlled by a timed relay. The checkers found that a 19 × 340-mm. vacuum-jacketed column fitted with a magnetically operated liquid takeoff and packed with ¼-in. glass Raschig rings was sufficient for carrying out the distillation. The checkers, using a reflux ratio of 2.7 to 1 throughout the distillation, found the total time required to be 19 hours.

Since the required separations are not difficult, any reasonably efficient fractionating column may be used.

3. Other soluble non-volatile bases may be used.

4. It is best to keep the temperature of the distilland below 125–150°, because pyrolysis of the product becomes progressively more serious at higher temperatures. The pressure is reduced to a convenient value when the distilland temperature reaches 125°. For example, a pressure of 200 mm. will allow the condensation of the [benzene](#) without resort to special cooling.

3. Discussion

[Acetone dibutyl acetal](#) has been prepared from [isopropenyl acetate](#) and [butanol](#),² from [butanol](#) and [isopropenyl butyl ether](#) obtained from the reaction of [butanol](#) with [propyne](#),³ and by orthoformic ester synthesis.^{4,5}

4. Merits of Preparation

The preparation described here is a modification of previously used alkoxyl interchange reactions, but it is more convenient because the use of the azeotrope-forming solvent permits the virtually complete removal of the by-product alcohol under mild conditions. The method is general for most primary and secondary alcohols, including those with functional groups which are stable under the mild conditions used.

References and Notes

1. The Dow Chemical Company, Texas Division, Freeport, Tex.
 2. W. J. Croxall, F. J. Glavis, and H. T. Neher, *J. Am. Chem. Soc.*, **70**, 2805 (1948).
 3. M. F. Shostakovskii and E. P. Gracheva, *Zhur. Obshch. Khim.*, **23**, 1320 (1953) [C.A., 48, 9899 (1954)].
 4. O. Grummitt and J. A. Stearns, Jr., *J. Am. Chem. Soc.*, **77**, 3136 (1955).
 5. C. A. MacKenzie and J. H. Stocker, *J. Org. Chem.*, **20**, 1695 (1955).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Benzene (71-43-2)

methanol (67-56-1)

cyclohexane (110-82-7)

butanol (71-36-3)

sodium methoxide (124-41-4)

isopropenyl acetate (108-22-5)

hexane (110-54-3)

Acetone dibutyl acetal,
Propane, 2,2-dibutoxy- (141-72-0)

acetone dimethyl acetal,
2,2-dimethoxypropane (77-76-9)

isopropenyl butyl ether

propyne (74-99-7)

p-toluenesulfonic acid (104-15-4)