



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.

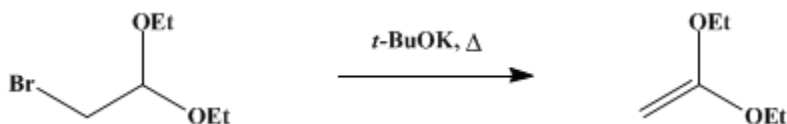
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.506 (1955); Vol. 23, p.45 (1943).

KETENE DIETHYLACETAL

[Ketene, diethyl ketal]



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1. Procedure

In a 2-l. round-bottomed flask, preferably fitted with an interchangeable ground-glass joint, are placed 650 g. (820 ml.) of absolute *tert*-butyl alcohol (Note 1) and 39.1 g. (1 gram atom) of potassium (Note 2). A reflux condenser is attached to the flask and the mixture is refluxed until all the potassium is dissolved (about 8 hours). The solution is allowed to cool slightly, and 198 g. (1 mole) of bromoacetal, together with some boiling chips (Note 3) is quickly added. A cream-colored precipitate of potassium bromide begins to deposit immediately. The flask is attached at once to a closely indented 46-cm. Vigreux column, equipped with a glass insulating jacket and a total-reflux partial take-off still head¹ (Note 4), and the *tert*-butyl alcohol is distilled from an oil bath (about 120–130°) at the rate of 25 drops per minute with a reflux ratio at the still head of about 6:1. This operation requires 16–18 hours (Note 5), and at the end of this time the temperature of the oil bath is raised to 160° and maintained there until no more alcohol comes over. The bath is then lowered and allowed to cool while the pressure within the fractionating system is very gradually reduced to 200 mm. and held there by a barostat (Note 6).

A small amount of the alcohol comes over at 51–52° /200 mm., and then, after the heating bath is replaced, 4–6 ml. of an intermediate fraction distils. This is followed by a fraction which boils at 83–86°/200 mm. and which is collected as pure ketene acetal. A total of 78–87 g. is obtained (67–75%). The major portion is collected while the temperature of the bath is 120–140°, and the remainder is obtained by raising the bath temperature to 170–180°.

Ketene acetal is best stored in a bottle made of alkaline glass which is preferably new and dusted with sodium *tert*-butoxide (Note 7). The glass stopper should be very well greased. Even with these precautions a small amount of a voluminous precipitate of the white polymer will develop.

2. Notes

1. The *tert*-butyl alcohol is refluxed over quicklime, distilled, and then redistilled over 1 g. of potassium per 100 g. of the alcohol. Improved yields of ketene acetal are obtained from *tert*-butyl alcohol that has been recovered from a previous preparation of the acetal.
2. The potassium should be cut into pieces sufficiently small to pass through the neck of the flask. Sodium in *tert*-butyl alcohol can be used, but it is necessary to carry out the subsequent reaction at 125° in sealed tubes. The amount of *tert*-butyl alcohol specified is sufficient to provide for complete solution of the potassium as the *tert*-butoxide.
3. An ebullator tube through which dry nitrogen was drawn has been used for the subsequent distillation under reduced pressure, but it is far more advantageous to use about six boiling chips. Because of its rapid reaction with water, ketene acetal must be protected from moisture of the air.
4. The still head described by Whitmore and Lux¹ is most satisfactory for controlling this distillation. The tube leading from the take-off of the column is attached to the receiver through a fraction cutter protected from moisture by a large tube of calcium chloride. The checkers replaced the Vigreux column by a 50-cm. column filled with glass helices and surrounded by a heating jacket. With this column the removal of the *tert*-butyl alcohol was complete in 5–6 hours.
5. A slower rate of fractionation does not result in an increased yield, but interrupted fractionation

results in a decreased yield.

6. A good barostat is necessary. Control of the reduced pressure by adjusting a "leak" in the system is entirely unsatisfactory, for, as a result of a small increase in pressure, the liquid ceases to boil, the column drains, and the boiling chips are rendered ineffective. The barostat used by the submitters is essentially that described by Ellis² in which the relay is replaced by the thermionic relay described by Waddle and Saeman.³

7. The column and apparatus should not be washed with acid cleaning solution because the glass surface is left acidic and it then catalyzes the polymerization of ketene acetal.⁴ A thin coating of the polymer on the walls of the apparatus is not detrimental. If polymer must be removed, it is best done by dissolving it in a 10% solution of hydrochloric acid in acetone; a deep red solution results.

3. Discussion

Ketene acetal may be prepared by the action of potassium *tert*-butoxide on iodoacetal⁵ or bromoacetal.⁴

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 684](#)

References and Notes

1. Whitmore and Lux, *J. Am. Chem. Soc.*, **54**, 3451 (1932).
2. Ellis, *Ind. Eng. Chem., Anal. Ed.*, **4**, 318 (1932).
3. Waddle and Saeman, *Ind. Eng. Chem., Anal. Ed.*, **12**, 225 (1940); Ferry, *Ind. Eng. Chem., Anal. Ed.*, **10**, 647 (1938).
4. Johnson, Barnes, and McElvain, *J. Am. Chem. Soc.*, **62**, 964 (1940).
5. Beyerstedt and McElvain, *J. Am. Chem. Soc.*, **58**, 529 (1936).

Appendix

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

Bromoacetal

absolute *tert*-butyl alcohol

iodoacetal

[hydrochloric acid](#) (7647-01-0)

[nitrogen](#) (7727-37-9)

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

[sodium](#) (13966-32-0)

[potassium bromide](#) (7758-02-3)

[potassium](#) (7440-09-7)

Ketene diethylacetal (2678-54-8)

Ketene, diethyl ketal

ketene acetal

tert-butyl alcohol (75-65-0)

potassium tert-butoxide (865-47-4)

tert-butoxide

sodium tert-butoxide (865-48-5)