



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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7-*t*-BUTOXYNORBORNADIENE

[2,5-Norbornadiene, 7-*tert*-butoxy-]



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1. Procedure

A 2-l. three-necked flask, fitted with stirrer, condenser, dropping funnel, and an arrangement for maintenance of an inert atmosphere, is charged with a mixture of 300 g. (3.26 moles) of [norbornadiene](#) ([Note 1](#)) and 0.650 g. (4.53 mmoles) of [cuprous bromide](#) ([Note 2](#)) in 500 ml. of [benzene](#) ([Note 3](#)). Dry [nitrogen](#) is introduced continuously, and, after the flask contents are brought to reflux, 245 g. (1.26 mole) of *t*-butyl perbenzoate ([Note 4](#)), dissolved in 100 ml. of [benzene](#), is added over approximately 1 hour to the stirred mixture. The solution immediately becomes blue or blue-green. The modest heat of reaction requires the application of some heat throughout the reaction period in order to maintain reflux. After the addition is completed, the solution is heated at the reflux temperature for an additional 30 minutes ([Caution!](#) ([Note 5](#))).

The mixture is cooled to room temperature, transferred to a 4-l. separatory funnel, and washed with three 300-ml. portions of saturated brine, to remove copper salts, and three 300-ml. portions of 10% aqueous [sodium hydroxide](#), to remove [benzoic acid](#) ([Note 6](#)). The [benzene](#) solution is then washed with 150 ml. of brine and is dried over anhydrous [sodium sulfate](#).

The dried solution is transferred to a 2-l. flask fitted with a Claisen head attached to a 30-cm. Vigreux column. [Benzene](#) is removed fairly rapidly at about 200 mm. so that the [benzene](#) boils at 45–50° ([Note 7](#)). After removal of most of the [benzene](#), the pressure is slowly lowered to 10–15 mm.; a negligible amount of fore-run is obtained before the product begins to distil at about 65° at 15 mm. The product is collected until the temperature reaches 80–85° at the same pressure ([Note 8](#)). The yield of 7-*t*-butoxynorbornadiene is 42–51 g. (20–25%, based on *t*-butyl perbenzoate) ([Note 9](#)). Gas-phase chromatographic analysis of the product shows it to be about 95% pure. Greater purity can be obtained, if required, by fractionation through a spinning band column; the pure product is collected at 70–72° (14 mm.) ([Note 10](#)).

2. Notes

1. [Norbornadiene](#) as supplied by Shell Chemical Co. is used without further purification. Distillation of the [norbornadiene](#) immediately before use gives no change in yield of 7-*t*-butoxynorbornadiene.
2. The [cuprous bromide](#) was used as obtained from E. H. Sargent Co. One instance of an ineffective batch of [cuprous bromide](#) from another source has been reported to the submitters. [Cuprous bromide](#) is only slightly soluble in the [benzene](#) solution. Greater amounts of catalyst have no effect on the yield of product.
3. Baker and Adamson or Merck reagent grade [benzene](#) was used.
4. *t*-Butyl perbenzoate was used as received from Lucidol Division of Wallace and Tiernan Co., Buffalo, New York.
5. Normally, after this time, the *t*-butyl perbenzoate is completely reacted. It is advisable, however, to check for its presence because distillation of a crude product containing some perester can lead to an explosion. *t*-Butyl perbenzoate absorbs strongly in the infrared at 5.65–5.70 μ , and examination of the

infrared spectrum of the benzene solution is a sufficiently sensitive test. No difficulty has ever been encountered during reactions with norbornadiene. However, unreacted *t*-butyl perbenzoate has caused a minor explosion with another, less reactive olefin.

6. Unless the copper salts are removed first, the basic wash frequently produces a thick emulsion which requires considerable time to settle.

7. The benzene is removed at reduced pressure to minimize heating of the product which consists chiefly of high-boiling esters. The last trace of benzene and norbornadiene is removed at a lower pressure.

8. *7-t*-Butoxynorbornadiene is collected over this wide temperature range since the last portion of the distillate is super-heated because of the large quantity of high-boiling materials remaining in the pot. No other reaction products boil in the same range, and GPC analysis has shown the last fraction of distillate to be nearly as pure as the middle cut.

9. This reaction has been conducted under a variety of conditions, but the yield of *7-t*-butoxynorbornadiene has never been less than 20% or greater than 26%.

10. Infrared (μ , CCl₄): 6.48 (w), 7.20 (m), 7.35 (s), 7.61 (m), 9.05 (s), 13.7 (s). The absorptions at 6.48 (double-bond stretch) and 13.7 (*cis* double bond C-H out-of-plane deformation) are very characteristic of the norbornadiene nucleus. N.m.r. spectrum (CCl₄): τ = 3.56 (m), 3.70 (m), 6.77 (m), 6.38 (m), 8.94 (s).

3. Discussion

The only method reported² for the preparation of *7-t*-butoxynorbornadiene is that described here. The general reaction of *t*-butyl perbenzoate with various olefins has been described by many investigators.³ When benzoyl peroxide is used in place of *t*-butyl perbenzoate under similar conditions, *7*-benzoxynorbornadiene is obtained in 38% yield; it is said to be more easily hydrolyzed to the alcohol than *7-t*-butoxynorbornadiene.⁴

4. Merits of the Preparation

7-t-Butoxynorbornadiene provides a convenient route to 7-substituted norbornenes and norbornadienes including *anti*-7-norbornenol,² 7-norbornadienyl acetate,² 7-norbornadienol,² 7-chloronorbornadiene,⁵ 7-methylnorbornadiene,⁶ and 7-phenylnorbornadiene.⁶ These compounds are useful in studies of the nature of chemical bonding.^{5,7}

References and Notes

1. Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.
 2. P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).
 3. M. S. Kharasch, G. Sosnovsky, and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959); D. B. Denney, D. Z. Denney, and G. Feig, *Tetrahedron Letters*, No. 15, 19 (1959); J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).
 4. H. Tanida and T. Tsuji, *Chem. Ind. (London)*, 211 (1963).
 5. P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962).
 6. P. R. Story and S. R. Fahrenholtz, Unpublished results.
 7. S. Winstein and C. Ordonneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).
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Appendix

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

brine

t-butyl perbenzoate

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

Benzoic acid (65-85-0)

cuprous bromide (7787-70-4)

benzoyl peroxide (94-36-0)

norbornadiene

7-benzoxynorbornadiene

7-norbornadienyl acetate

7-norbornadienol

7-chloronorbornadiene

7-methylnorbornadiene

7-phenylnorbornadiene

7-t-BUTOXYNORBORNADIENE,
2,5-Norbornadiene, 7-tert-butoxy- (877-06-5)

anti-7-norbornenol