



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.

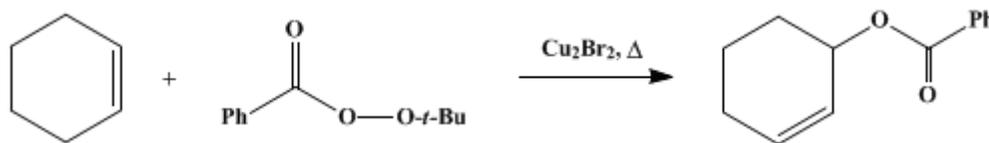
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.70 (1973); Vol. 48, p.18 (1968).

3-BENZOYLOXYCYCLOHEXENE

[2-Cyclohexen-1-ol, benzoate]



Submitted by Knud Pedersen, Preben Jakobsen, and Sven-Olov Lawesson¹.

Checked by R. Schöllhorn and R. Breslow.

1. Procedure

Caution! This reaction should be carried out behind a safety screen. The solvent removal and product distillation steps should also be carried out behind a screen to minimize danger due to contamination of the product with undetected peroxides.

A 250-ml., three-necked, round-bottomed flask equipped with a sealed mechanical stirrer, a reflux condenser, and a pressure-equalizing dropping funnel is set up for conducting a reaction in an atmosphere of **nitrogen** by fitting into the top of the condenser a T-tube attached to a low-pressure supply of **nitrogen** and to a mercury bubbler. In the flask are placed 41 g. (0.50 mole) of **cyclohexene** and 0.05 g. (0.00035 mole) of **cuprous bromide**, and the mixture is heated in an oil bath at 80–82°. When the temperature of the mixture reaches that of the oil bath, 40 g. (0.21 mole) of *t*-butyl perbenzoate (**Note 1**) is added dropwise with stirring over a 1-hour period, during which the color of the now homogeneous solution becomes blue. Stirring and heating are continued for an additional 3.5 hours (**Note 2**). The cooled reaction mixture is washed with two 50-ml. portions of dilute aqueous **sodium carbonate** to remove **benzoic acid** (**Note 3**). The remaining organic phase is washed with water until neutral and dried over anhydrous **sodium sulfate**. The excess of **cyclohexene** is removed by distillation under reduced pressure, and the residue (**Note 4**) is distilled through a short Vigreux column to give 29–33 g. (71–80%) of **3-benzoyloxycyclohexene**, b.p. 97–99° (0.15 mm.), n_D^{20} 1.5376–1.5387 (**Note 5**).

2. Notes

1. *t*-Butyl perbenzoate is supplied by Lucidol Division, Wallace and Tiernan, Inc., Buffalo 5, New York, or L. Light and Co., Ltd., Colorbrook, Bucks, England. The Lucidol product contains 98% *t*-butyl perbenzoate.
2. The progress of the reaction can most conveniently be followed by periodic examination of the infrared spectrum of the mixture ($\nu_{C=O}$ for peroxybenzoate: 1775 cm^{-1}). After all of the perester has been added, *ca.* 3 hours is required for its consumption.
3. After acidification of the aqueous phase 1.5–2 g. of **benzoic acid** can be isolated.
4. It is recommended that an infrared spectrum be run on the residue before the distillation to check for the absence of perester (**Note 2**).
5. The same yield is obtained when the scale is increased threefold.

3. Discussion

The procedure is that of Kharasch, Sosnovsky, and Yang.²

4. Merits of the Preparation

The reaction described is of considerable general utility for the preparation of benzoyloxy derivatives of unsaturated hydrocarbons.^{2,3,4,5,6,7,8} Reactions of *t*-butyl perbenzoate with various other

classes of compounds in the presence of catalytic amounts of copper ions produce benzoyloxy derivatives. Thus this reaction can also be used to effect one-step oxidation of saturated hydrocarbons,^{9,10} esters,^{5,11} dialkyl and aryl alkyl ethers,^{12,13,14} benzylic ethers,^{11,15} cyclic ethers,^{13,16} straight-chain and benzylic sulfides,^{12,17,18,19} cyclic sulfides,^{11,19} amides,¹¹ and certain organosilicon compounds.²⁰ Reviews^{20,21} of these reactions are available.

References and Notes

1. Department of Chemistry, University of Aarhus, 8000 Aarhus C., Denmark.
2. M. S. Kharasch, G. Sosnovsky, and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959).
3. D. B. Denney, D. Z. Denney, and G. Feig, *Tetrahedron Lett.*, No. **15**, 19 (1959).
4. A. L. J. Beckwith and G. W. Evans, *Proc. Chem. Soc.*, 63 (1962).
5. G. Sosnovsky and N. C. Yang, *J. Org. Chem.*, **25**, 899 (1960).
6. B. Cross and G. H. Whitham, *J. Chem. Soc.*, 1650 (1961).
7. J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 774 (1962).
8. D. Z. Denney, A. Appelbaum, and D. B. Denney, *J. Am. Chem. Soc.*, **84**, 4969 (1962).
9. M. S. Kharasch and A. Fono, *J. Org. Chem.*, **23**, 324 (1958).
10. T. I. Wang, Ph.D. Thesis, University of Chicago, 1962.
11. C. Berglund and S.-O. Lawesson, *Arkiv Kemi*, **20**, 225 (1963).
12. S.-O. Lawesson, C. Berglund, and S. Grönwall, *Acta Chem. Scand.*, **15**, 249 (1961).
13. G. Sosnovsky, *Tetrahedron*, **13**, 241 (1961).
14. S.-O. Lawesson and C. Berglund, *Arkiv Kemi*, **17**, 465 (1961).
15. S.-O. Lawesson and C. Berglund, *Arkiv Kemi*, **16**, 287 (1960).
16. S.-O. Lawesson and C. Berglund, *Arkiv Kemi*, **17**, 475 (1961).
17. S.-O. Lawesson and C. Berglund, *Acta Chem. Scand.*, **15**, 36 (1961).
18. G. Sosnovsky, *Tetrahedron*, **18**, 15 (1962).
19. G. Sosnovsky, *Tetrahedron*, **18**, 903 (1962).
20. G. Sosnovsky and S.-O. Lawesson, *Angew. Chem.*, **76**, 218 (1964).
21. S.-O. Lawesson and G. Schroll, in S. Patai, "The Chemistry of Carboxylic Acids and Esters," Wiley-Interscience, London, 1969, p. 669.

Appendix

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

t-butyl perbenzoate

Cyclohexene (110-83-8)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

Benzoic acid (65-85-0)

cuprous bromide (7787-70-4)

3-Benzoyloxycyclohexene,

2-Cyclohexen-1-ol, benzoate (3352-93-0)

Copyright © 1921-2005, Organic Syntheses, Inc. All Rights Reserved