



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](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.

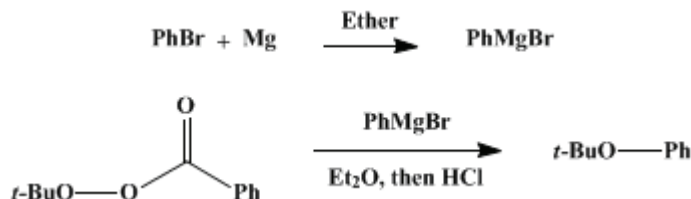
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.924 (1973); Vol. 45, p.89 (1965).*

## PHENYL *t*-BUTYL ETHER

[Ether, *tert*-butyl phenyl]

### [Method I]



Submitted by Christer Frisell and Sven-Olov Lawesson<sup>1</sup>.

Checked by William G. Dauben and Gilbert H. Berezin..

### 1. Procedure

A 1-l., three-necked, round-bottomed flask equipped with a sealed mechanical stirrer, a reflux condenser, and a 500-ml. pressure-equalized dropping funnel is arranged 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. The flask is dried by warming with a soft flame as a slow stream of **nitrogen** is passed through the system. In the cooled flask a solution of **phenylmagnesium bromide** is prepared from 13 g. (0.53 g. atom) of **magnesium turnings**, 79 g. (0.5 mole, 53.6 ml.) of **bromobenzene**, and 200 ml. of anhydrous **ether**.

After the preparation of **phenylmagnesium bromide** is complete, the ethereal solution is cooled in an ice bath and 200 ml. of anhydrous **ether** is added. A solution of 58.3 g. (0.3 mole, 56 ml.) of *t*-butyl perbenzoate (**Note 1**) in 120 ml. of anhydrous **ether** is added, dropwise, with stirring over a 30-minute period, and the stirring is continued for an additional 5 minutes.

The reaction mixture is poured carefully into a cold solution of 40 ml. of concentrated **hydrochloric acid** in 1 l. of water. The ethereal layer is separated, and the aqueous layer is extracted twice with 150-ml. portions of **ether**. The combined organic layers are extracted with three 25-ml. portions of 2*M* **sodium hydroxide** solution, washed with water until the washings are neutral, and then dried over anhydrous **magnesium sulfate** (**Note 2**) and (**Note 3**). The dried solution is concentrated and the product distilled under reduced pressure, b.p. 57–59°/7 mm. The yield of **phenyl *t*-butyl ether** is 35–38 g. (78–84%),  $n_D^{25}$  1.4870–1.4880. This synthetic process is applicable to the preparation of other *t*-butyl ethers (**Note 4**).

### 2. Notes

1. *t*-Butyl perbenzoate is supplied by Lucidol Division, Wallace and Tiernan Inc., Buffalo 5, New York, or L. Light & Co., Ltd., Colnbrook, Bucks, England. The Lucidol product contains 98% *t*-butyl perbenzoate.

2. The ethereal solution should be tested for peroxides as follows: A few milligrams of **sodium iodide**, a trace of **ferric chloride**, and 3 ml. of glacial **acetic acid** are placed in a test tube and 2 ml. of the ether solution added carefully. When unconsumed perbenzoate is present, a yellow ring is formed immediately between the two phases. If a positive test is obtained, the acid and base treatments should be repeated.

3. By acidification of the **sodium hydroxide** solution, 29–32 g. of **benzoic acid** (80–90%) is obtained.

4. The same general method<sup>2</sup> has been used by the submitters to prepare *o*-tolyl *t*-butyl ether,<sup>3</sup> *m*-tolyl *t*-butyl ether,<sup>3</sup> benzyl *t*-butyl ether,<sup>3</sup> and *p*-anisyl *t*-butyl ether.

### 3. Discussion

The method presented is essentially that described by Lawesson and Yang.<sup>4</sup> Phenyl *t*-butyl ether has been prepared by acid-catalyzed condensation of isobutylene and phenol<sup>5</sup> by reaction of diphenyliodonium chloride with potassium *t*-butoxide,<sup>6</sup> and by the next procedure in this volume.<sup>7</sup>

#### 4. Merits of Preparation

The synthesis of *t*-butyl ethers by the reaction of Grignard reagents with *t*-butyl perbenzoate appears to have considerable generality (Note 4), and the perester is a stable, readily available material.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 926](#)

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### References and Notes

1. Department of Chemistry, University of Uppsala, Uppsala, Sweden.
  2. S.-O. Lawesson and G. Schroll, in S. Patai, "The Chemistry of Carboxylic Acids and Esters," Wiley-Interscience, London, 1969, p. 669.
  3. S.-O. Lawesson and C. Frisell, *Arkiv Kemi*, **17**, 287 (1961).
  4. S.-O. Lawesson and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 4230 (1959).
  5. D. R. Steven, *J. Org. Chem.*, **20**, 1232 (1955).
  6. F. M. Beringer, P. S. Forgione, and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960).
  7. M. R. V. Sahyun and D. J. Cram, *this volume*, p. 926.
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### Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

*t*-butyl perbenzoate

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

[acetic acid \(64-19-7\)](#)

[ether \(60-29-7\)](#)

[sodium hydroxide \(1310-73-2\)](#)

[magnesium turnings \(7439-95-4\)](#)

[phenol \(108-95-2\)](#)

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

[Benzoic acid \(65-85-0\)](#)

[bromobenzene \(108-86-1\)](#)

[ferric chloride \(7705-08-0\)](#)

Phenylmagnesium bromide (100-58-3)

sodium iodide (7681-82-5)

magnesium sulfate (7487-88-9)

isobutylene (9003-27-4)

diphenyliodonium chloride (1483-72-3)

potassium t-butoxide (865-47-4)

m-tolyl t-butyl ether

benzyl t-butyl ether

PHENYL t-BUTYL ETHER,  
Ether, tert-butyl phenyl (6669-13-2)

o-tolyl t-butyl ether (15359-96-3)

p-anisyl t-butyl ether (15360-00-6)