



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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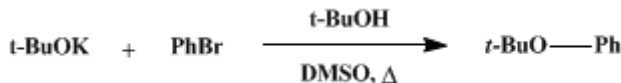
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.926 (1973); Vol. 41, p.91 (1961).

PHENYL *t*-BUTYL ETHER

[Ether, *t*-butyl phenyl]

[Method II]



Submitted by Melville R. V. Sahyun and Donald J. Cram¹.

Checked by William G. Dauben and David J. Ellis.

1. Procedure

In a loosely stoppered 1-l. round-bottomed flask are placed 37.5 g. (48 ml.) of *t*-butyl alcohol, 150 ml. of dimethyl sulfoxide (Note 1), and a Teflon[®]-coated magnetic stirring bar. The solution is heated in an oil bath which is placed on a combination magnetic stirrer-hotplate. When the temperature of the mixture reaches 125–130°, 75 g. (0.67 mole) of alcohol-free potassium *t*-butoxide (Note 2) and (Note 3) is added, the stopper is replaced loosely, and the mixture is stirred. When all the potassium *t*-butoxide is in solution, the stopper is removed, 25 g. (0.159 mole, 17 ml.) of bromobenzene is added in one portion to the hot solution, and an air condenser fitted with a drying tube is rapidly placed on the flask. The solution immediately turns dark brown, and an extremely vigorous, exothermic reaction occurs. After 1 minute the reaction mixture is poured into 500 ml. of water. The aqueous solution is saturated with sodium chloride and extracted with four 200-ml. portions of ether (Note 4). The ether extract is washed with three 100-ml. portions of water and dried over anhydrous potassium carbonate. The ether is distilled at atmospheric pressure on a steam bath to leave 17–18 g. of crude phenyl *t*-butyl ether (Note 5). The brown oil is distilled to yield 10–11 g. (42–46%) of pure phenyl *t*-butyl ether, b.p. 45–46° (2 mm.), m.p. –17 to –16°, *n*²⁵_D 1.4860–1.4890 (Note 6). The ether may be hydrolyzed readily to phenol (Note 7).

2. Notes

1. "Baker Analyzed" dimethylsulfoxide, which is freshly opened and dry to Karl Fischer reagent, is used without further purification.
2. Commercial potassium *t*-butoxide is used directly as obtained from the Mine Safety Appliance Reserach Corp., Callery, Pennsylvania.
3. This amount of potassium *t*-butoxide is not soluble in the dimethylsulfoxide at a lower temperature. An excess of base over *t*-butyl alcohol is necessary to the reaction, and a high concentration of *t*-butyl alcohol (3.3*M*) considerably improves the yield of product desired.
4. The aqueous residue from the extraction can be acidified and extracted to yield phenol which is purified by chromatography on a silica gel column, with an eluant solution composed of 95% pentane and 5% ether by volume. The purified phenol weighs 4.3 g. (29% of the theoretical amount) and is obtained as long needles.
5. The crude material also contains some polymeric material and traces of solvent. Gas chromatography indicates that the phenyl *t*-butyl ether is 60–70% pure at this point.
6. The checkers found their product to contain 0.5–1.0% bromobenzene. Careful redistillation is required to free the product of this impurity.
7. Phenyl *t*-butyl ether is swirled with 6*N* hydrochloric acid until solution is completed. The solution is then saturated with sodium chloride and extracted with ether to yield phenol, identifiable as the tribromide.

3. Discussion

The procedure described here is based on a method outlined by Cram, Rickborn, and Knox.² The

method is not a general one for the preparation of a substituted [phenyl *t*-butyl ether](#) because an aryne intermediate is involved. It appears that aryl fluorides undergo direct substitution to yield unrearranged aryl *t*-butyl ethers. Alternative methods for preparation of these ethers are listed on [page 924](#).

4. Merits of the Preparation

This reaction sequence illustrates how the rates of many basecatalyzed reactions can be enhanced greatly by substitution of [dimethylsulfoxide](#) for the usual hydroxylic solvents.³ Other examples of the enhanced reactivity of anions in [dimethylsulfoxide](#) are found in Wolff-Kishner reductions and Cope elimination reactions.⁵ The present reaction illustrates the generation of an aryne intermediate from [bromobenzene](#).⁴

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 924](#)
- [Org. Syn. Coll. Vol. 6, 683](#)
- [Org. Syn. Coll. Vol. 6, 991](#)

References and Notes

1. Department of Chemistry, University of California, Los Angeles 24, California.
 2. D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).
 3. D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *J. Am. Chem. Soc.*, **83**, 3678 (1961).
 4. D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Am. Chem. Soc.*, **84**, 1734 (1962).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[alcohol-free potassium *t*-butoxide](#)

[potassium carbonate \(584-08-7\)](#)

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

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

[sodium chloride \(7647-14-5\)](#)

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

[Pentane \(109-66-0\)](#)

[dimethyl sulfoxide,
dimethylsulfoxide \(67-68-5\)](#)

[t-butyl alcohol \(75-65-0\)](#)

potassium t-butoxide (865-47-4)

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

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