



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.

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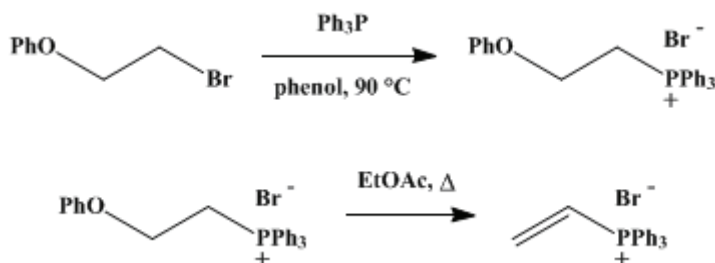
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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VINYL TRIPHENYLPHOSPHONIUM BROMIDE

[Phosphonium bromide, triphenylvinyl-]



Submitted by Edward E. Schweizer and Robert D. Bach¹.

Checked by François X. Garneau and Peter Yates.

1. Procedure

Caution! Because phenol and its solutions are corrosive, rubber gloves should be used in the following operations. The product, vinyl triphenylphosphonium bromide, has been found to induce a sneezing, allergic reaction and contact with it should be avoided.

In a 1-l. three-necked flask is placed 1 lb. of reagent grade phenol (Note 1), 100 g. (0.50 mole) of β -bromophenetole, and 131 g. (0.50 mole) of triphenylphosphine (Note 2). The flask is equipped with a sealed stirrer, a thermometer, and a reflux condenser fitted with a calcium chloride drying tube. The mixture is stirred and heated to $90^\circ \pm 3^\circ$ (Note 3) and kept at this temperature for 48 hours.

The solution is cooled to room temperature and added slowly (during 45 minutes) from a dropping funnel to vigorously stirred anhydrous ether (3 l.) in a 4-l. beaker. Material that adheres to the sides of the beaker is scraped down with a long steel spatula, and the mixture is filtered by suction. The solid product is transferred into a second 3-l. portion of anhydrous ether, and the mixture is stirred vigorously for 15 minutes and filtered by suction. The product is washed with three 250-ml. portions of warm anhydrous ether.

The white crystalline residue of crude phenoxyethyltriphenylphosphonium bromide (Note 4) is placed in a 3-l. two-necked flask equipped with a sealed stirrer and a reflux condenser fitted with a calcium chloride drying tube. Reagent grade (Note 5) ethyl acetate (1.5 l.) is added, and the solution is stirred under reflux for 24 hours. The mixture is cooled to room temperature, and the ethyl acetate layer is decanted (or filtered if the salt is crystalline). This procedure is repeated until the filtered salt, vinyl triphenylphosphonium bromide, melts at 186° and higher (Note 6).

After the final filtration the product is washed with two 100-ml. portions of ethyl acetate and two 100-ml. portions of anhydrous ether and dried for 24 hours at 80° . The dried, analytically pure vinyl triphenylphosphonium bromide, m.p. $186\text{--}190^\circ$, weighs 122–158 g. (66–86%).

2. Notes

1. The checkers found that it was important to use phenol free of colored impurities; in a run in which phenol, m.p. $39.5\text{--}41^\circ$, with a slight rose tinge was used the yield of product was reduced to 56%.
2. The β -bromophenetole was obtained from Aldrich Chemical Co.; the triphenylphosphine was obtained from M and T Chemicals, Inc., or Carlisle Chemical Works, Reading, Ohio, and recrystallized once from anhydrous ether (with filtration).
3. It is important that the temperature does not rise above 95° . There is a slight exotherm on initial heating that may necessitate the removal of the heating mantle in order to maintain a temperature below

95°.

4. Pure samples of this material may be obtained by using [acetic acid](#) as solvent instead of [phenol](#).²
5. Because the vinyl salt reacts with [ethanol](#), and decomposition of the phenoxyethyl precursor is inhibited by [acetic acid](#),² reagent grade [ethyl acetate](#) is recommended.
6. Four treatments have always been necessary. The residue has always crystallized on cooling after the third treatment.

3. Discussion

The present procedure is that described by the submitters.² Vinyl triphenylphosphonium bromide has also been prepared by dehydrobromination of 2-bromoethyltriphenylphosphonium bromide, but no preparative details or yields have been disclosed.³

4. Merits of the Preparation

This salt has been used as a general reagent for the preparation of a large number of heterocyclic and carbocyclic systems.^{4,5,6,7,8,9,10,11,12,13,14,15,16,17} A variety of salts of type $XCH_2CH_2P^+(C_6H_5)_3Br^-$ has been prepared from the vinyl salt by treatment with alcohols, [thiophenol](#), and [diethylamine](#).²

References and Notes

1. Department of Chemistry, University of Delaware, Newark, Delaware 19711.
2. E. E. Schweizer and R. D. Bach, *J. Org. Chem.*, **29**, 1746 (1964).
3. D. Seyferth, J. S. Fogel, and J. K. Heeren, *J. Am. Chem. Soc.*, **86**, 307 (1964).
4. E. E. Schweizer, *J. Am. Chem. Soc.*, **86**, 2744 (1964).
5. E. E. Schweizer and K. K. Light, *J. Am. Chem. Soc.*, **86**, 2963 (1964).
6. E. E. Schweizer, L. D. Smucker, and R. J. Votral, *J. Org. Chem.*, **31**, 467 (1966).
7. E. E. Schweizer and G. J. O'Neill, *J. Org. Chem.*, **30**, 2082 (1965).
8. E. E. Schweizer and K. K. Light, *J. Org. Chem.*, **31**, 870 (1966).
9. E. E. Schweizer and L. D. Smucker, *J. Org. Chem.*, **31**, 3146 (1966).
10. E. E. Schweizer and J. G. Liehr, *J. Org. Chem.*, **33**, 583 (1968).
11. E. E. Schweizer, J. Liehr, and D. J. Monaco, *J. Org. Chem.*, **33**, 2416 (1968).
12. E. E. Schweizer, W. S. Creasy, J. G. Liehr, M. E. Jenkins, and D. L. Dalrymple, *J. Org. Chem.*, **35**, 601 (1970).
13. E. E. Schweizer and C. S. Kim, *J. Org. Chem.*, **36**, 4033 (1971).
14. E. E. Schweizer and C. S. Kim, *J. Org. Chem.*, **36**, 4041 (1971).
15. E. E. Schweizer and C. M. Kopay, *J. Org. Chem.*, **37**, 1561 (1972).
16. S. Brandange and C. Lundin, *Acta Chem. Scand.*, **25**, 2447 (1971).
17. D. Johnson and G. Jones, *J. Chem. Soc.*, [PI] 840 (1972).

Appendix

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

[ethanol](#) (64-17-5)

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

[ethyl acetate](#) (141-78-6)

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

phenol (108-95-2)

diethylamine (109-89-7)

β -bromophenetole (589-10-6)

Thiophenol (108-98-5)

triphenylphosphine (603-35-0)

Vinyl triphenylphosphonium bromide,
Phosphonium bromide, triphenylvinyl- (5044-52-0)

phenoxyethyltriphenylphosphonium bromide

2-bromoethyltriphenylphosphonium bromide