Organic Syntheses

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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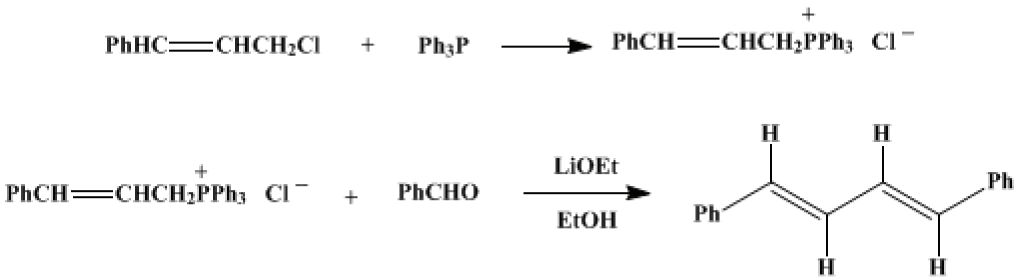
1,4-DIPHENYL-1,3-BUTADIENE

[1,3-Butadiene,1,4-diphenyl-]



Submitted by Richard N. McDonald and Tod W. Campbell[1].
Checked by M. S. Newman, R. Marshall, and W. N. White.

1. Procedure

A. *Triphenylcinnamylphosphonium chloride*. A mixture of 40 g. (0.26 mole) of (3-chloropropenyl) benzene (Note 1) and 92 g. (0.35 mole) of triphenylphosphine (Note 2) in 500 ml. of xylene is heated at reflux for 12 hours with stirring. The mixture is allowed to cool to about 60°, and the colorless crystalline product is filtered, washed with 100 ml. of xylene, and dried in a vacuum oven at about 20 mm. pressure and 60° to constant weight. The yield is 99–101 g. (91–93%), m.p. 224–226° (Note 3).

B. *1,4-Diphenylbutadiene*. To a solution of 60.0 g. (0.145 mole) of triphenylcinnamylphosphonium chloride and 16.4 g. (0.155 mole) of benzaldehyde in 200 ml. of ethanol (Note 4) is added 760 ml. of 0.2*M* lithium ethoxide in ethanol (Note 5) and (Note 6). After allowing this mixture to stand 30 minutes, 700 ml. of water is added (Note 7) and the colorless crystals are filtered, washed with 150 ml. of 60% ethanol, and dried in the vacuum oven at 65°. The yield of crystalline product, m.p. 153–156°, is 17.9–19.9 g. (60–67%) (Note 8). The product is the *trans-trans* isomer and is pure enough for most purposes (Note 9). Recrystallization from cyclohexane gives a product with m.p. 154–156°.

2. Notes

1. Eastman Organic Chemicals, white label grade, used without purification.
2. Commercial triphenylphosphine was used without further purification. Metal and Thermit Corp., Rahway, New Jersey, now offers this reagent for sale at a modest price.
3. The phosphonium salt can be recrystallized to analytical purity by dissolving in a small amount of boiling ethanol, adding ether at the boil until cloudy, and allowing the salt to crystallize in a refrigerator.
4. Commercial anhydrous ethanol was used throughout without further purification.
5. The lithium ethoxide solution is prepared by dissolving 1.40 g. of lithium wire in 1 l. of anhydrous ethanol.
6. A transient orange color is immediately formed, and it is replaced by crystallization of the product in about 1 minute.
7. Triphenylphosphine oxide is soluble in 60% aqueous ethanol; therefore it remains in the filtrate and affords no difficulty.
8. The yield can probably be increased by carrying out the reaction in an ether solvent with an alkyllithium as base, but the simplicity and relative ease of the conditions described appear to make the possible yield advantage secondary.
9. This procedure has been applied successfully to the synthesis of substituted bistyryls, i.e., 1-(*p*-tolyl)-4-phenylbutadiene (76%), 1-(4-methoxyphenyl)-4-phenylbutadiene (63%), and 1-(4-acetamidophenyl)-4-phenylbutadiene (61%), by using the corresponding substituted benzaldehydes.

3. Discussion

1,4-Diphenylbutadiene has been obtained from phenylacetic acid and cinnamaldehyde with lead oxide,[2] by the dehydrogenation of 1,4-diphenyl-2-butene with butyllithium,[3] and by the coupling reaction of benzenediazonium chloride and cinnamylideneacetic acid.[4] The present method[5] gives better yields than those previously reported, is adaptable to the preparation of a variety of substituted bistyryls, and is relatively easy to carry out.

References and Notes

1. Pioneering Research Division, Textile Fibers Department, E. I. du Pont de Nemours and Co., Wilmington, Delaware.
2. B. B. Corson, *Org. Syn.*, Coll. Vol. **2**, 229 (1943). This reference includes previous preparative methods.
3. H. Gilman and C. W. Bradley, *J. Am. Chem. Soc.*, **60**, 2333 (1938).
4. C. F. Koelsch and V. Boekelheide, *J. Am. Chem. Soc.*, **66**, 412 (1944).
5. T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1241. (1959).

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

ethanol	(64-17-5)
ether	(60-29-7)
lead oxide	
benzenediazonium chloride	
cyclohexane	(110-82-7)
benzaldehyde	(100-52-7)
Phenylacetic acid	(103-82-2)
xylene	(106-42-3)
cinnamaldehyde	
Lithium wire	(7439-93-2)
1,4-Diphenylbutadiene, 1,4-Diphenyl-1,3-butadiene, 1,3-Butadiene,1,4-diphenyl-	(886-65-7)
butyllithium	(109-72-8)
triphenylphosphine	(603-35-0)
triphenylphosphine oxide	(791-28-6)

(3-chloropropenyl) benzene (21087-29-6)

triphenylcinnamylphosphonium chloride

lithium ethoxide

1-(4-methoxyphenyl)-4-phenylbutadiene

1-(4-acetamidophenyl)-4-phenylbutadiene

1,4-diphenyl-2-butene

cinnamylideneacetic acid

1-(p-tolyl)-4-phenylbutadiene