



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.

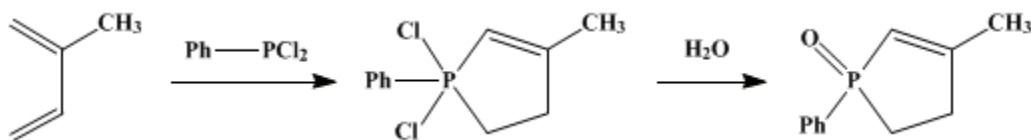
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.787 (1973); Vol. 43, p.73 (1963).*

## 3-METHYL-1-PHENYLPHOSPHOLENE OXIDE

### [Phospholene, 3-methyl-1-phenyl-, 1-oxide]



Submitted by W. B. McCormack<sup>1</sup>

Checked by S. N. Lewis and W. D. Emmons.

### 1. Procedure

A. *3-Methyl-1-phenylphospholene 1,1-dichloride*. A dry 1-l. suction flask (Note 1) is charged with 179 g. (1.00 mole) of dichlorophenylphosphine ( $n_D^{28}$  1.592; (Note 2)), 300 ml. (about 204 g., 3.0 moles) of commercial isoprene (Note 3), and 2.0 g. of Ionol<sup>®</sup> (Note 4). The flask is then stoppered, the side arm is sealed with tubing and a clamp, and the homogeneous solution is allowed to sit at room temperature in the back of a hood for 5–7 days. White solid is usually apparent within 2–4 hours, and after the reaction period the liquid phase is full of a white crystalline adduct, 1,1-dichloro-1-phenyl-3-methyl-1-phospha-3-cyclopentene. The granular adduct is crushed, slurried with petroleum ether, collected on a sintered glass Büchner funnel, and washed with petroleum ether; exposure to moisture of the air is minimized by covering the funnel with a clock glass (Note 5).

B. *3-Methyl-1-phenylphosphacyclopentene 1-oxide*. The adduct is hydrolyzed by stirring it into 700 ml. of ice water, and stirring is continued until essentially all of it is in solution (Note 6). The total amount of acid in the solution is determined by titrating an aliquot, and the solution is nearly neutralized by slow addition of about 93% of the theoretical amount of 30% sodium hydroxide with good stirring and sufficient ice to keep the temperature below 25°. The solution generally contains about 1.62 equivalents of acid, which calls for 150 ml. (1.50 equivalents) of 30% sodium hydroxide. The pH is then adjusted to 6.5 with sodium bicarbonate solution (Note 7). After saturation of the aqueous solution with sodium chloride, the product is extracted with three 250-ml. portions of chloroform. The chloroform extracts are combined, dried briefly over calcium sulfate, filtered, and concentrated at atmospheric pressure until the temperature of the liquid in the distillation flask is 130°. The residual liquid is fractionated through a 30-cm. packed column. A water aspirator is used initially to strip small amounts of low boilers at 100° (Note 8), and then a mechanical pump is used. There is a fore-shot of a partially solidifying oil, weight 2–3 g., b.p. 163–168°/0.6–0.7 mm. Then 110–120 g. (57–63%) of 3-methyl-1-phenyl-1-phospha-3-cyclopentene 1-oxide, b.p. 173–174°/0.7 mm., is collected. It is a viscous liquid of a very pale yellow color that solidifies to a white solid, m.p. 60–65° (Note 9). A small amount of residue remains (Note 10).

### 2. Notes

1. A suction flask provides a strong-walled reactor that is conveniently stored for the reaction period.
2. Commercial material (currently from Stauffer Chemical Company, Special Chemicals Division) is suitable after distillation.
3. Shell Chemical material (92% minimum purity) was used. It was noted by the checkers that redistilled isoprene gave slightly better yields. The excess isoprene serves both as a solvent and for mass action. Moreover, dichlorophenylphosphine tends to dissolve in the product, and excess isoprene, by extracting the solid, promotes completion of reaction.
4. Ionol<sup>®</sup> is a commercial antioxidant, 2,6-di-*tert*-butyl-*p*-cresol, manufactured by Shell Chemical Corp. Inhibitors appear to minimize formation of polymeric side products, although with isoprene the effect is often small.
5. Sometimes, as with less pure reagents or on heating, a viscous oil, red to dark in color, will form instead of a white solid. At other times the solid is rather gummy. In these cases, mixing with petroleum

ether as much as possible and decanting must suffice.

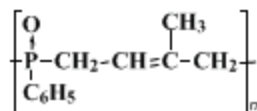
6. On occasion, gelatinous material is apparent; in time it usually dissolves or swells greatly.

7. The product is relatively sensitive to basic conditions, showing both polymerization and addition of water. Therefore alkaline conditions must be avoided. Neutralization serves to convert [monophenylphosphinic acid](#) (formed by hydrolysis of unreacted, unextracted [dichlorophenylphosphine](#)) to the monosodium salt, thereby preventing its subsequent extraction from water along with the [phosphine oxide](#).

8. The crude mixtures all have strong odors of aromatic phosphines. Some of this odor presumably arises from disproportionation of [monophenylphosphinic acid](#) to [phenylphosphine](#). It is recommended that manipulations be carried out with rubber gloves to prevent transfer of these rather durable odors to the skin, and that all equipment be washed with a bleach such as Clorox<sup>®</sup> before it is taken from the hood.

9. The distilled product can be used as a catalyst, although it usually has a relatively strong [phenylphosphine](#) odor. It is quite deliquescent, and it has not been satisfactorily recrystallized. If rigorous purification and deodorization are desired, the product is dissolved in water, a small amount of [hydrogen peroxide](#) is added to oxidize the phosphines, the solution is reneutralized, saturated with salt, and extracted with [chloroform](#), and the product is refractionated. One cycle is normally enough. Pure product is essentially odorless, very hygroscopic, and soluble in polar solvents.

10. This residue is mostly the linear copolymer of nearly 1:1 composition. On occasion it can be present in substantial amounts, especially if higher temperatures are used to increase the reaction rate.



### 3. Discussion

[3-Methyl-1-phenylphosphacyclopentene 1-oxide](#) has been prepared only as described here.<sup>2</sup>

### 4. Merits of the Preparation

The reaction given here has been described before as a general reaction,<sup>2</sup> and there can be a wide variety of alkyl, aryl, and halo substituents on the diene and [phosphorus](#). Dibromophosphines are appreciably more reactive than dichlorophosphines. If a free-radical catalyst is used instead of an inhibitor, the copolymers can be made in good yield.<sup>3</sup> The 1,4-addition of dichlorophosphines to 1,3-dienes is of theoretical interest because of its analogy to the well-known 1,4-addition of [sulfur dioxide](#) to 1,3-dienes.

The unsaturated cyclic phosphine oxides are active catalysts for the conversion of aryl isocyanates to carbodiimides.<sup>4</sup> The polymeric material<sup>3</sup> and the saturated cyclic [phosphine oxides](#)<sup>5</sup> are also catalysts but are less active. The unsaturated cyclic phosphine oxides show properties analogous to those of the unsaturated cyclic sulfones from dienes and [sulfur dioxide](#) in that the double bond is quite reactive to basic reagents and relatively resistant to acidic reagents. Physically these cyclic phosphine oxides are stable to over 300°, are very powerful hydrogen bond acceptors, and are excellent solvents for polar materials.

The most recent review<sup>6</sup> summarizes the chemistry of these materials.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 501](#)

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### References and Notes

1. Contribution No. 317, Organic Chemicals Department, E. I. du Pont de Nemours and Co.,

Wilmington, Delaware.

2. W. B. McCormack, U.S. Patent 2,663,737 (1953) [*C. A.*, **49**, 7601a (1955)].
  3. W. B. McCormack, U.S. Patent 2,671,079 (1954) [*C. A.*, **48**, 6738c (1954)].
  4. T. W. Campbell and J. J. Verbanc, U.S. Patent 2,853,473 (1958) [*C. A.*, **53**, 10126e (1959)]; T. W. Campbell and J. J. Monagle, *this volume*, p. 504.
  5. W. B. McCormack, U.S. Patent 2,663,739 (1953) [*C. A.*, **49**, 7602f (1955)].
  6. F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, and Bismuth," 2nd Edition, Wiley-Interscience, New York, 1970, pp. 31–61.
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

petroleum ether

Ionol

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

sodium bicarbonate (144-55-8)

sodium chloride (7647-14-5)

sulfur dioxide (7446-09-5)

PHOSPHORUS (7723-14-0)

calcium sulfate (7778-18-9)

hydrogen peroxide (7722-84-1)

phosphine (7723-14-0)

ISOPRENE (78-79-5)

dichlorophenylphosphine (644-97-3)

phosphine oxide

3-Methyl-1-phenylphospholene oxide,  
Phospholene, 3-methyl-1-phenyl-, 1-oxide,  
3-Methyl-1-phenylphosphacyclopentene 1-oxide (707-61-9)

3-methyl-1-phenyl-1-phospha-3-cyclopentene 1-oxide

monophenylphosphinic acid (121-70-0)

phenylphosphine (638-21-1)

2,6-di-tert-butyl-p-cresol (128-37-0)

3-Methyl-1-phenylphospholene 1,1-dichloride (17154-12-0)

1,1-dichloro-1-phenyl-3-methyl-1-phospha-3-cyclopentene