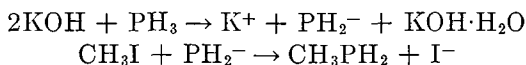


## 25. METHYLPHOSPHINE



Submitted by WILLIAM L. JOLLY\*

Checked by ROBERT PAINE, JR.†

Both methylphosphine (this synthesis) and dimethylphosphine (the following synthesis) are considerably stronger Lewis bases than phosphine, and their reactions with various Lewis acids,<sup>1</sup> including boranes,<sup>2,3</sup> have been the subject of recent studies. Both methylphosphine and dimethylphosphine are readily oxidized by air, and thus can serve as sources of methylphosphinous (methylphosphinic) acid,  $\text{CH}_3\text{PHO}(\text{OH})$ , and dimethylphosphinic acid,  $(\text{CH}_3)_2\text{PO}(\text{OH})$ .<sup>1</sup>

A commonly used synthetic method for these substituted phosphines involves the deprotonation of phosphine<sup>2,4</sup> (or methylphosphine<sup>2</sup>) by a sodium-ammonia solution, followed by treatment with a methyl halide. More recently,<sup>3</sup> methylphosphine has been produced by the reduction of methyldichlorophosphine (unfortunately, not a readily available compound) by lithium hydroaluminate. The present method is essentially the deprotonation-methylation procedure, but instead of sodium-ammonia solutions, relatively easily handled KOH–dimethyl sulfoxide suspensions are used.

**Procedure**

■ **Caution.** *Phosphine and methylphosphine are toxic materials which must be handled with great care, using vacuum-line manipulation. Dimethyl sulfoxide should not be allowed to contact the skin because it is absorbed very rapidly.*

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A magnetic stirring bar, 30 g. of potassium hydroxide powder, and 40 ml. of dimethyl sulfoxide are placed in a 200-ml. three-necked round-bottomed flask with standard-taper joints. One side neck is stoppered, the other is fitted with a small dropping funnel, and the main neck is fitted with an adapter connected to a 0- to 760-mm. manometer and a stopcock leading to a vacuum line. The joints are greased with Dow-Corning silicone grease. The flask is thoroughly evacuated while the mixture is stirred, and the stopcock is then closed. About 0.012 mole of pure phosphine<sup>5</sup> is transferred to a 300-ml. bulb connected to the vacuum line just beyond the stopcock, and the stopcock is opened so as to allow the phosphine to be absorbed by the stirred potassium hydroxide suspension. The dimethyl sulfoxide becomes yellow because of the formation of the  $\text{PH}_2^-$  ion. When the manometer indicates that about 99% of the phosphine has been absorbed (after about 25 minutes), the system is again thoroughly evacuated. The stopcock is closed, a solution of 1.0 ml. (0.016 mole) of methyl iodide in 10 ml. of dimethyl sulfoxide is placed in the dropping funnel, and a trap between the stopcock and the vacuum pump is immersed in liquid nitrogen.

About 2 ml. of the methyl iodide solution is added to the stirred mixture, and after about 10 seconds, the stopcock is opened for a minute. This process is repeated until the dimethyl sulfoxide solution is colorless. The crude methylphosphine which collects in the liquid-nitrogen-cooled trap is then purified by fractional condensation in traps cooled to  $-112^\circ$  ( $\text{CS}_2$  slush),  $-130^\circ$  (*n*-pentane slush), and  $-196^\circ$  (liquid nitrogen). The material which collects in the  $-112$  and  $-196^\circ$  traps is discarded. About 0.009 mole (75% yield) of purified methylphosphine collects in the  $-130^\circ$  trap.

### Properties

Methylphosphine is an evil-smelling material which is probably very poisonous. The vapor pressure may be represented<sup>4</sup> by the equation  $\log P(\text{mm.}) = 7.402 - 1158/T$ , where  $T = ^\circ\text{K}$ .

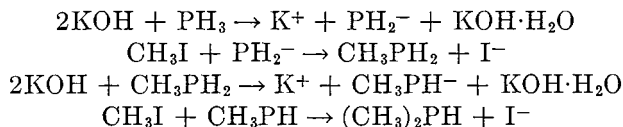
The extrapolated boiling point is  $-17.1^{\circ}$ , and the vapor pressures at  $-78.5^{\circ}$  (28 mm.),  $-63.5^{\circ}$  (73 mm.), and  $-45.2^{\circ}$  (210 mm.) may be used as criteria of purity. The infrared spectrum of the gas has been reported;<sup>6</sup> the appearance of a band at  $1252\text{ cm.}^{-1}$  indicates the presence of methyl iodide, and the appearance of a band at  $1170\text{ cm.}^{-1}$  indicates the presence of dimethyl ether.

The methylphosphine prepared by this procedure has a vapor pressure at  $-78.5^{\circ}$  (Dry Ice slush) of 29 mm. The principal impurity is dimethyl ether, estimated by mass spectrometry and infrared spectrometry to amount to less than 1%.

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## 26. DIMETHYLPHOSPHINE



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The following procedure is adaptable to the synthesis of 0.05 mole, or less, of dimethylphosphine. The procedure described on p. 157 may be used for the synthesis of larger quantities.

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