2,2-Dimethyl-1,3-propanediol bis(cyclic 2,2-dimethyltrimethylene phosphorothionate) (IX). 2,2-Dimethyl-1,3-propanediol bis(cyclic 2,2-dimethyltrimethylene phosphite) (18.4 g., 0.05 mole), sulfur (3.2 g., 0.1 mole), and 70 ml. of benzene were mixed with stirring. A weakly exothermic reaction occurred. The reaction mixture was stirred at 25° for 48 hr., refluxed for 8 hr., and then cooled. A cream-colored solid (3.3 g.) crystallized from the benzene solution. Recrystallization of this material from benzene gave white crystals, m.p. 163–164°.

Anal. Calcd. for $C_{15}H_{30}O_6P_2S_2$: P, 14.33; S, 14.83. Found: P, 14.13; S, 14.74.

KINGSPORT, TENN.

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Preparation and Characterization of Vinyldichlorophosphine, Vinyldimethylphosphine, and Ethyldimethylphosphine[1,2]

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The air and moisture sensitive compound vinyldichlorophosphine (b.p. 104°/760 mm.) is readily obtained by heating a mixture of phosphorus trichloride and divinylmercury. Treatment of methylmagnesium chloride in diglyme with vinyldichlorophosphine afforded vinyldimethylphosphine (b.p. 69.0°/760 mm.) Ethyldimethylphosphine (b.p. 73.3°/760 mm.) was similarly prepared from ethyldichlorophosphine. The vapor tensions of four phosphines are reported.

As part of a study[5] on the relative electron-pair donor power of several organophosphines it was necessary to prepare and characterize vinyldimethylphosphine and ethyldimethylphosphine. The latter compound has been reported by Collie,[6] but has not been mentioned in the chemical literature since its discovery in 1888. Ethyldimethylphosphine was prepared by us by the sequence of reactions:

$$3PCl_3 + PbEt_4 \longrightarrow 3EtPCl_2 + PbCl_2 + EtCl \qquad (a)$$

$$EtPCl_2 + 2MeMgCl \xrightarrow[\text{diglyme}^7]{} EtPMe_2 + 2MgCl_2 \qquad (b)$$

Reaction (a) was carried out exactly as described by Kharasch *et al.*[8] The normal boiling point of ethyldimethylphosphine is 11° less than that reported earlier.[6] The hitherto unreported compound vinyldimethylphosphine was obtained from the reaction between vinyldichlorophosphine and methylmagnesium chloride. Before this reaction could be carried out, however, it was necessary to prepare a vinyldihalophosphine. Although trivinylarsine and trivinylstibine undergo redistribution to the vinylhalo derivatives when mixed with the trichlorides or tribromides of the respective elements, trivinylphosphine and phosphorus trihalides yield only black solids.[9] Similarly, excellent yields of vinylhaloarsines were obtained by Seyferth[9,10] by treating arsenic trihalides with dibutyldivinyltin, but when the "mixed" redistribution method was applied to phosphorus trihalides the desired vinylhalophosphines were not obtained. It is still possible that vinyldihalophosphines could be obtained from these reactions by empirically varying the experimental techniques until the correct conditions are found, but meanwhile, as described in the experimental section, the recently discovered divinylmercury[11] provides a ready route to such compounds.

$$(CH_2{:}CH)_2Hg + PCl_3 \xrightarrow{\text{heat}} CH_2{:}CHPCl_2 + CH_2{:}CHHgCl$$

Vinyldichlorophosphine (b.p. 104°/760 mm.) is very sensitive to air and to moisture. Even when sealed in evacuated ampoules it will decompose unless the ampoules have been thoroughly baked during evacuation. The gas-phase infrared spectrum of vinyldichlorophosphine has been studied[3] over the region 650–3500 cm.$^{-1}$. It shows the typical absorption C—H stretches at 3050 and 3110 cm.$^{-1}$; an overtone of a 968 cm.$^{-1}$ band at 1930 cm.$^{-1}$; C—H deformations at 1400, 1324 and 968 cm.$^{-1}$; and the P—C stretch frequency at 728 and 671

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[2] Presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959.

[3] Taken from the thesis of H. D. Kaesz submitted to the Graduate School of Arts and Sciences, Harvard University, in partial fulfillment of the requirements of the Ph.D. degree. Other parts of the dissertation are published elsewhere.

[4] Public Health Predoctoral Fellow of the National Heart Institute.

[5] H. F. Kaesz and F. G. A. Stone, abstracts of papers presented at the 135th Meeting of the American Chemical Society held in Boston, Mass., April 1959, p. 11M.

[6] N. Collie, *Trans. Chem. Soc.*, **53**, 714 (1888).

[7] Diglyme is the commercial name for diethyleneglycol dimethyl ether (Ansul Chemical Co.).

[8] M. S. Kharasch, E. V. Jensen, and S. Weinhouse, *J. Org. Chem.*,**14**, 429 (1949).

[9] L. Maier, D. Seyferth, F. G. A. Stone, and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 5884 (1957).

[10] D. Seyferth, Technical Report, Office of Naval Research Contract No. Nonr-1866(13), February, 1957.

[11] B. Bartocha, F. E. Brinckman, H. D. Kaesz, and F. G. A. Stone, *Proc. Chem. Soc.*, 116 (1958); B. Bartocha and F. G. A. Stone, *Z. Naturforsch.*, **13b**, 347 (1958); G. F. Reynolds, R. E. Dessy, and H. H. Jaffé, *J. Org. Chem.*, **23**, 1217 (1958).

TABLE I

PHYSICAL CONSTANTS OF THE PHOSPHINES

Compound	$\log_{10}P(mm.) = -A/T + B$ A	B	ΔH Vap. at B.P., Kcal. Mole^{-1}	Trouton Constant, E.U.	Boiling Point[a]
$(Et)(Me)_2P$	1712	7.850	7.83	22.4	71.2[b]
$(CH_2{:}CH)(Me)_2P$	1693	7.846	7.75	22.7	67.9[c]
Et_3P	2065	8.035	9.45	23.6	127.5[d]
$(CH_2{:}CH)_3P$	1944	7.868	8.90	22.8	116.6[e]

[a] By extrapolation of vapor pressure equation. [b] Reference (6) reports a normal boiling point of 84°. Observed in this work 73.3°. [c] Observed in this work 69.0°. [d] Observed 127.5°, by F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935). [e] Observed in this work, 58.1°/100 mm. Calcd. 58.1°/100 mm.

cm.$^{-1}$. The P—Cl stretch normally occurs at 430 to 585 cm.$^{-1}$ and would not be seen on this spectrum. The infrared spectra of a variety of phosphorus compounds have been correlated in a review by Daasch and Smith.[12]

Vapor tensions of ethyldimethylphosphine and vinyldimethylphosphine are listed in Table II. The vapor tensions of triethylphosphine do not appear to have been reported previously, so these are also given in Table II. Vapor tensions of trivinylphosphine have been reinvestigated by us (Table II) because those previously obtained by Stone[9] are incorrect. Trivinylphosphine was first reported by Maier[9] who obtained it, after some difficulty, from vinylmagnesium bromide and phosphorus trichloride. Unfortunately unknown to Maier *et al.*[9] the vinyl bromide obtained commercially and used to make the vinyl Grignard contained appreciable quantities (*circa* 20%) of ethyl bromide with the result that the trivinylphosphine prepared contained significant amounts of triethylphosphine and perhaps ethylvinylphosphines. It is of course impossible to detect triethylphosphine in trivinylphosphine by elemental analysis, or to separate effectively the two compounds by distillation. Infrared spectra differences, however, will detect as little as 3% ethyl contamination of vinyl-metal or -metalloid compounds.[13] The infrared spectrum of triethylphosphine has strong bands at 1468 cm.$^{-1}$, 1423 cm.$^{-1}$, and 1380 cm.$^{-1}$. Bands at these frequencies do not appear in the spectrum of trivinylphosphine.

The constants which may be derived from the results presented in Table II are listed in Table I.

It is interesting to note that a tetrahydrofuran solution of trivinylphosphine, unlike a tetrahydrofuran solution of trimethylphosphine, does not give an immediate red precipitate with carbon disulfide. Vinyldimethylphosphine is intermediate between trivinyl- and trimethylphosphine in its behavior toward carbon disulfide. Triphenylphosphine, on the other hand, gives no precipitate with carbon disulfide. Rate of formation of a red adduct from an organophosphine and carbon disulfide appears to correlate roughly with the Lewis base strength of the phosphine, even though the carbon disulfide adducts might not be simple molecular addition compounds.

EXPERIMENTAL

Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

Vapor tensions of the phosphines. Representative vapor tensions were determined with a tensimeter[14] and are given in Table II. Temperature measurements were made with N.B.S. calibrated thermometers graduated in 1/10ths from 0° to 100°. For each temperature setting 0.5 hr. was allowed for thermal equilibration, the temperature being controlled to within ±0.1°. An oil bath was used to heat the tensimeter. The bath tank had windows of parallel plate glass. Pressure readings were taken with a George & Becker Co. (London) cathetometer with a vernier calibrated to 0.02 mm.

TABLE II

VAPOR TENSIONS OF SOME ORGANOPHOSPHINES

t	$P_{mm.}$ Obsd.	$P_{mm.}$ Calcd.	t	$P_{mm.}$ Obsd.	$P_{mm.}$ Calcd.
		Ethyldimethylphosphine			
0.1	38.4	38.7	14.7	81.4	80.3
4.5	48.2	48.6	19.2	99.7	99.1
9.5	63.0	62.4	24.2	124.3	124.4
		Vinyldimethylphosphine			
0.0	44.5	44.5	14.3	90.5	90.4
4.4	55.7	55.7	18.9	111.8	111.9
9.5	71.8	71.8			
		Triethylphosphine			
41.8	30.0	30.2	62.5	76.6	76.5
48.8	42.0	41.9	70.5	106.3	106.4
50.1	44.5	44.4	80.0	154.0	154.3
		Trivinylphosphine			
39.7	45.2	45.2	60.7	111.0	111.2
46.9	62.5	62.4	67.5	145.5	145.3
54.3	85.6	85.6			

Preparation of phosphines by the Grignard technique. In the preparation of organophosphines by reaction between phosphorus trichloride and Grignard reagents, best yields are obtained using a large excess of *chloro*-Grignards, and the two reagents should be brought together at as low

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[12] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

[13] H. D. Kaesz and F. G. A. Stone, *Spectrochimica Acta*, in press.

[14] A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, 59, 780 (1937).

a temperature[15] as is possible, down to −78°. Thus, the procedure described by Maier *et al.*[9] for the preparation of trivinylphosphine involving simultaneous addition of vinylmagnesium bromide and phosphorus trichloride is unnecessary when vinylmagnesium chloride is used instead of vinylmagnesium bromide. Normal Grignard procedures may be followed and yields are good. Vinylmagnesium chloride (1.11 mole in 1 liter tetrahydrofuran) with phosphorus trichloride (0.254 mole in 350 ml. tetrahydrofuran) gave, after hydrolysis with saturated ammonium chloride solution, a 55% yield of trivinylphosphine (b.p. 58.1°/100 mm.). Before the vinyl chloride was used to make the Grignard, its purity (better than 99%) was established by gas-phase chromatography.

Reaction between ethyldichlorophosphine and methylmagnesium chloride. Methylmagnesium chloride (2.75 mole) was formed in tetrahydrofuran, and this solvent subsequently exchanged for 1 l. of diglyme.[16] This was done by removing the tetrahydrofuran *in vacuo*, with stirring to avoid bumping. A lubricated Tru-bore stirrer will withstand a pressure differential of one atmosphere. Prepurified nitrogen was readmitted to the system and 500 ml. of the new solvent added. Solvent removal was continued. This process of taking the Grignard down almost to dryness was repeated twice, using fresh increments of diglyme, until the infrared spectrum of the distillate showed the absence of tetrahydrofuran. The Grignard in diglyme was then cooled at about −60° and treated with ethyldichlorophosphine[8] (60 g., 0.458 mole) dissolved in 350 ml. of thoroughly dried and degassed diglyme. The mixture was not hydrolyzed. Liquid was removed from the reaction flask under reduced pressure and collected at −78°. Treatment with dry hydrogen chloride gave a white solid[17] which was washed with diethyl ether, and dried by pumping *in vacuo*. Free dimethylethylphosphine was released from its phosphonium salt by treatment with dimethylamine. The phosphine was treated for several days with resublimed P_2O_5 to remove traces of moisture and dimethylamine. The dimethylethylphosphine was carefully fractionated (b.p. 73.3 ± 0.1/760 mm.). Yield, 32 g. (78%).

Anal. Calcd. for $C_4H_{11}P$: C, 53.31; H, 12.31. Found: C, 53.49; H, 12.49.

Reaction between divinylmercury and phosphorus trichloride. Freshly distilled phosphorus trichloride (420 g., 3.06 mole), together with 60 ml. of dry degassed mineral oil, were placed under nitrogen in the flat bottomed flask, suitable for magnetic stirring, and equipped with a thermometer well, dropping funnel, and reflux condenser. A 145 g. (0.57 mole) sample of divinylmercury[11] was placed in the pressure-equalized addition funnel, and the flask was warmed by a heating mantle until gentle reflux took place. Divinylmercury was then slowly added, and stirring begun. The temperature of the reaction flask was maintained between 65° and 85° during addition of divinylmercury, and the reflux was continued for 1 hr. after all the mercury compound had been added. The contents of the flask turned dark brown. On cooling, the reaction flask was attached to a distillation apparatus, and about 250 ml. of excess phosphorus trichloride carefully removed at 200 mm. pressure. Previous experience had shown that if distillation is completed in the presence of the brown solids, only a small quantity of desired material is obtained. Therefore, the remaining liquid was transferred *in vacuo* at room temperature to a 100 ml. distillation flask cooled to −78°, and containing 15–25 ml. of degassed mineral oil. Toward the end of the transfer, the reaction flask was heated to 100° to ensure complete transfer of liquid product. The contents of the 100 ml. distillation flask were carefully fractionated, yielding vinyldichlorophosphine (36 g.) (b.p. 63.4 ± 0.2/200 ± 1 mm.) in 50% yield.

Anal. Calcd. for $C_2H_3PCl_2$: C, 18.63; H, 2.34; Cl, 55.00. Found: C, 18.45; H, 2.22; Cl, 54.80.

Reaction between vinyldichlorophosphine and methylmagnesium chloride. This reaction was carried out in a manner similar to that described above for the preparation of ethyldimethylphosphine. Methylmagnesium chloride (1.12 mole in 1250 ml. of diglyme) was treated with vinyldichlorophosphine (36 g., 0.28 mole) in 300 ml. of thoroughly dried and degassed diglyme. The mixture was not hydrolyzed, crude vinyldimethylphosphine being removed *in vacuo* and condensed at −78°. This material was fractionated giving pure vinyldimethylphosphine (8.7 g.) (b.p. 69.0°/760 mm.) in 35% yield.

Anal. Calcd. for C_4H_9P: C, 54.53; H, 10.30. Found: C, 54.30; H, 10.30.

Acknowledgment. We are indebted to the Ethyl Corp. for providing us with a sample of tetraethyllead which was used to prepare the ethyldichlorophosphine mentioned in this paper.

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[15] We are indebted to Dr. J. Chatt for emphasizing the importance of low temperature, although our own studies on trivinylphosphine led us tentatively to the same conclusion.

[16] Solvent exchange was carried out in order that the synthesis could be continued in a solvent whose boiling point was very different from that of the phosphine being prepared.

[17] Due to the extreme hygroscopic nature of phosphonium salts, the HCl must be rigorously dry. Traces of moisture will form a water solution of the phosphonium salt, which must then be dried by heating near 100°, under reduced pressure. It is necessary that the product at this point be a crystalline salt to permit ether washing and filtration.