Poly(tertiary phosphines and arsines). X. The Syntheses of Methylated Poly(tertiary phosphines)[1,2]

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Abstract: Novel methylated poly(tertiary phosphines) have been prepared mainly by the conversion of a P–H bond to a $PCH_2CH_2P(CH_3)_2$ unit through base-catalyzed addition to $CH_2{=}CHP(S)(CH_3)_2$ followed by desulfurization with $LiAlH_4$ in boiling dioxane. Thus the di(tertiary phosphine) $(C_6H_5)_2PCH_2CH_2P(CH_3)_2$ can be prepared from $(C_6H_5)_2PH$ and $CH_2{=}CHP(S)(CH_3)_2$. The tri(tertiary phosphine) $C_6H_5P[CH_2CH_2P(CH_3)_2]_2$ can be prepared similarly from $C_6H_5PH_2$ and $CH_2{=}CHP(S)(CH_3)_2$. The tri(tertiary phosphine) $CH_3P[CH_2CH_2P(C_6H_5)_2]_2$ can be prepared either from $(C_6H_5)_2PH$ and $CH_3P(S)(CH{=}CH_2)_2$ or by the base-catalyzed addition of CH_3PH_2 to $(C_6H_5)_2PCH{=}CH_2$. The completely aliphatic tri(tertiary phosphine) $CH_3P[CH_2CH_2P(CH_3)_2]_2$ can be prepared either from CH_3PH_2 and $CH_2{=}CHP(S)(CH_3)_2$ or from $(CH_3)_2PH$ and $CH_3P(S)(CH{=}CH_2)_2$. The linear tetra(tertiary phosphine) $(CH_3)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(CH_3)_2$ can be prepared from $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ and $CH_2{=}CHP(S)(CH_3)_2$. The completely aliphatic tripod tetra(tertiary phosphine) $P[CH_2CH_2P(CH_3)_2]_3$ can be prepared from $(CH_3)_2PH$ and $(CH_2{=}CH)_3PS$ or from $(CH_3)_2PCH_2CH_2PH_2$ and $CH_2{=}CHP(S)(CH_3)_2$. However, $LiAlH_4$ reduction of the adduct $P[CH_2CH_2P(S)(CH_3)_2]_3$ from PH_3 and $CH_2{=}CHP(S)(CH_3)_2$ in boiling dioxane results in hydrogenolysis rather than sample desulfurization to give the unusual di(tertiary)-secondary triphosphine $HP[CH_2CH_2P(CH_3)_2]_2$. The penta(tertiary phosphine) $[(CH_3)_2PCH_2CH_2]_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(CH_3)_2$ can be prepared from $C_6H_5P(H)CH_2CH_2PH_2$ and $CH_2{=}CHP(S)(CH_3)_2$. The hexa(tertiary phosphine) $[(CH_3)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(CH_3)_2]_2$ can be prepared from $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2$ and $CH_2{=}CHP(S)(CH_3)_2$. The proton and phosphorus-31 nmr spectra of these new poly(tertiary phosphines) are described.

The first paper of this series[4] describes the preparation of phenylated poly(tertiary phosphines) in which the phosphorus atoms are linked by $-CH_2CH_2-$ bridges with the remaining positions on each phosphorus atom occupied by phenyl groups. Subsequent papers[5-7] describe extensive series of transition metal complexes formed by these phosphines.

The phenylated poly(tertiary phosphines)[8] were ideal synthetic objectives to use for the development of reaction sequences for building up complex structures with PCH_2CH_2P units since the simpler ones are relatively air-stable crystalline solids which can be handled and purified by conventional techniques. Detailed study of their metal complexes poses some major problems, however. Many of the metal complexes are only sparingly soluble and therefore difficult to study by nmr. Even in cases where proton nmr spectra can be obtained, neither the phenyl groups nor the CH_2CH_2 bridges give unequivocal structural information. The low solubility of some metal complexes prevents the use of column chromatography for their isolation and purification.

Methylated poly(tertiary phosphines) offer several advantages over their phenylated analogs: more soluble metal complexes which are more readily purified and studied by nmr spectroscopy, a good proton nmr probe since each type of methyl group leads to a sharp, readily resolved doublet, and smaller steric requirements which should make possible additional types of metal complexes. The basic objective of the present research was to develop methods for synthesizing methylated poly(tertiary phosphines).

Our syntheses of phenylated poly(tertiary phosphines)[4,8] use the base-catalyzed addition of a phosphorus–hydrogen bond across the carbon–carbon double bond of a vinylphosphine to construct the basic PCH_2CH_2P building block by the reaction

$$P\text{-}H + CH_2{=}CHP \longrightarrow PCH_2CH_2P$$

Vinylphosphines, particularly $(C_6H_5)_2PCH{=}CH_2$, are required in large quantities. Fortunately, these vinylphosphines can be made easily.[9]

An analogous approach to methylated poly(tertiary phosphines) would require large quantities of $(CH_3)_2PCH{=}CH_2$ and $CH_3P(CH{=}CH_2)_2$, which are difficult to prepare and handle. The required intermediates $CH_2{=}CHPCl_2$[10] and $(CH_3)_2PCl$[11] are air-sensitive, malodorous, and much more difficult to prepare than $(C_6H_5)_2PCl$. In addition, $(CH_3)_2PCH{=}CH_2$ (bp 68° (760 mm)) is so volatile that it is difficult to separate from the reaction mixture, particularly if the usual tetrahydrofuran is used as a solvent. These difficulties indicate a need for preparations of methylated poly(tertiary phosphines) which avoid the use of trivalent methylvinylphosphines.

The most readily available derivative containing a $(CH_3)_2P$ unit is tetramethylbiphosphine disulfide, $(CH_3)_2P(S)P(S)(CH_3)_2$, which can be obtained in one step from methylmagnesium halides and $PSCl_3$.[12] We have developed an efficient procedure for converting tetramethylbiphosphine disulfide into dimethylvinylphosphine sulfide, $(CH_3)_2P(S)CH{=}CH_2$, without involving any organophosphorus compounds of high volatility or air-sensitivity. The $(CH_3)_2P(S)CH{=}CH_2$ can be considered as a "protected" form of dimethylvinylphosphine.

The addition of phosphorus–hydrogen bonds to the carbon–carbon double bond in dimethylvinylphosphine sulfide proceeds easily in good yield in the presence of the usual potassium *tert*-butoxide catalyst to give partially sulfurized methylated poly(tertiary phosphines), which are interesting compounds themselves since they contain both tricoordinate and tetracoordinate phosphorus atoms in the same molecule; this structural feature is known[13] but rather rare. Removal of the blocking sulfur atoms with $LiAlH_4$ in boiling dioxane gives the sulfur-free methylated poly(tertiary phosphines) in good yields.

This paper describes details for the syntheses of methylated tri-, tripod tetra-, and hexa(tertiary phosphines) of potential interest to coordination chemists. In addition, applications of this new synthetic method for the preparations of novel di-, tri-, linear tetra-, and penta(tertiary phosphines) with various combinations of methyl and phenyl substituents on the "free" positions of the trivalent phosphorus atoms in the poly(tertiary phosphine) network are also described.

Table I. Proton Nmr Spectra of the New Methylphosphorus Derivatives Described in This Paper

		Proton nmr spectrum, τ			
Compound	Medium	C_6H_5	CH_2CH_2	CH_3	Other
$Me_2P(S)(CH{=}CH_2)$	$CDCl_3$			8.22 d (13)	$CH_2{=}CH$: 3.5–3.8 m, 4.11 dd (11, 4)
$MeP(S)(CH{=}CH_2)_2$	Neat			8.00 d (13)	$CH_2{=}CH$: 3.0–4.0 m
$SP(CH{=}CH_2)_3$	$CDCl_3$				$CH_2{=}CH$: 3.04, 3.38 m, 3.86 dd (11, 5)
$Ph_2PCH_2CH_2P(S)Me_2$	$CDCl_3$	2.66 m	7.64 m, 8.16 m	8.36 d (13)	
$Ph_2PCH_2CH_2PMe_2$	Neat	2.68 m, 2.88 m	7.94 m, 8.66 m	9.19 d (2.8)	
$PhP[CH_2CH_2P(S)Me_2]_2$	$CDCl_3$	2.75	8.15	8.35 d (12) 8.37 d (12)	
$PhP(CH_2CH_2PMe_2)_2$	Neat	2.58 m, 2.81 d	8.28 m, 8.70 m	9.10 d (2.3) 9.12 d (2.5)	
$MeP(S)(CH_2CH_2PPh_2)_2$	$CDCl_3$	2.68 m	7.80 m, 8.24 m	8.49 d (12)	
$MeP(CH_2CH_2PPh_2)_2$	$CDCl_3$	2.68 m	7.97 q (8), 8.56 m	9.01 d (1.7)	
$MeP(S)(CH_2CH_2PMe_2)_2$	CH_2Cl_2		8.44 br	Me_2P: 8.97 d (2.6) MeP: 8.47 d (13)	
$MeP[CH_2CH_2P(S)Me_2]_2$	$CDCl_3$			Me_2P: 8.30 d (13) MeP: 8.94 d (3)	
$MeP(CH_2CH_2PMe_2)_2$	CH_2Cl_2		~8.5 br	Me_2P: 9.02 d (2.8) MeP: 9.02 d (2.8)	
$[Me_2P(S)CH_2CH_2P(Ph)CH_2{-}]_2$	$CDCl_3$	2.76	~8.2 m	8.38 d (12) 8.40 d (12)	
$[Me_2PCH_2CH_2P(Ph)CH_2{-}]_2$	C_6D_6	2.62 m, 2.93 m	~8.3 m, 8.75 br	9.27 d (2.5) 9.29 d (2.6)	
$[Me_2P(S)CH_2CH_2]_2PCH_2CH_2PMe_2$	CH_2Cl_2		8.2–8.6 m	$Me_2P(S)$– 8.33 d (13) Me_2P–: 9.00 d (2.5)	
$P(CH_2CH_2PMe_2)_3$	CH_2Cl_2		8.66 m	9.06 d (2.5)	
$HP(CH_2CH_2PMe_2)_2$	C_6H_6		8.4–8.6 br	9.10 d (3)	PH: 6.85 br, d (~190)
$Me_2PCH_2CH_2P(Ph)CH_2CH_2P(CH_2CH_2PMe_2)_2$	C_6D_6	2.71 br, 2.9 br	8.4 br, 8.7 br	9.13 d (3)	
$Me_2PCH_2CH_2[P_2C_2H_4][CH_2CH_2P(S)Me_2]_3$	CH_2Cl_2		8.1–8.6 m	$Me_2P(S)$–: 8.31 d (13) Me_2P–: 9.00 d (2.5)	
$[(Me_2PCH_2CH_2)_2PCH_2{-}]_2$	Neat		~8.6 br	9.03 d (2.8)	

Table II. Phosphorus-31 Nmr Spectra of Some Methylphosphorus Derivatives

		Phosphorus-31 nmr (ppm) upfield from external 85% H_3PO_4				
Compound	Medium	PhP or Ph_2P	CH_3P	$(CH_3)_2P$	$P(CH_2\text{-}CH_2{-})_3$	P–H
$Ph_2PCH_2CH_2PMe_2$	Neat	+13.2 dt (26, 7)		+47.7 d (26)		
$PhP(CH_2CH_2PMe_2)_2$	Neat	+17.6		+47.9 d (23)		
$MeP(CH_2CH_2PPh_2)_2$	CH_2Cl_2	+13.1	+32.6			
$MeP(S)(CH_2CH_2PMe_2)_2$	CH_2Cl_2		−46.0	+46.5 d (26)		
$MeP(CH_2CH_2PMe_2)_2$	CH_2Cl_2		+34.3 t (21)	+48.6 d (21)		
$P(CH_2CH_2PMe_2)_3$	Neat			+48.0 d (22)	+19.6	
$HP(CH_2CH_2PMe_2)_2$	Neat			+48.8 d (19)		+56.7 d (193)
$Me_2PCH_2CH_2P(Ph)CH_2CH_2P(CH_2CH_2PMe_2)_2$	C_6D_6	+17.4		+48.5 d (22)	+19.6	
$[(Me_2PCH_2CH_2)_2PCH_2{-}]_2$	Neat			+48.0 d (18)	+19.5	

Experimental Section

Microanalyses and molecular weight determinations by vapor pressure osmometry were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga., and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Proton nmr spectra (Table I) were taken as pure liquids or in the indicated solvents and were recorded either at 100 MHz on a Varian HA-100 spectrometer or at 60 MHz on a Perkin-Elmer Hitachi R-20 spectrometer. Phosphorus-31 nmr spectra (Table II) were taken on the pure liquids or in concentrated dichloromethane solutions and recorded at 40.5 MHz on a Varian HA-100 specrometer. Spectroscopic measurements on solutions of methylated poly(tertiary phosphines) in chlorinated solvents (particularly $CHCl_3$ and $CDCl_3$) must be done on freshly prepared solutions, since chlorinated solvents react slowly with methylated poly(tertiary phosphines) upon standing at room temperature.

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling air-sensitive organophosphorus compounds and the potassium *tert*-butoxide catalyst, and (c) filling evacuated vessels containing potentially air-sensitive materials. When necessary, a polyethylene glove bag was used to provide the nitrogen atmosphere. The amounts of the potassium *tert*-butoxide catalyst were estimated by volume on the tip of a spatula in order to avoid weighing and possible exposure to hydrolysis. A three-necked flask with a fritted disk and stopcock at the bottom was used for the nitrogen-atmosphere filtrations of ethereal solutions of trivalent organophosphorus compounds obtained after hydrolysis of $LiAlH_4$ reactions. All of the reactions discussed in this paper were carried out in an efficient hood using an aqueous calcium hypochlorite trap to decompose the effluent vapors before passing them into the hood exhaust.

Tetrahydrofuran and dioxane were purified by distillation under nitrogen over sodium benzophenone ketyl immediately before use.

Starting Materials. Vinyl bromide (Matheson, East Rutherford, N. J.), dimethyl methylphosphonate (Aldrich, Milwaukee, Wis.), lithium aluminum hydride (Columbia Organics, Columbia, S. C.), potassium *tert*-butoxide (MSA Research Corp., Evans City, Pa.), and aluminum phosphide (Alfa, Beverly, Mass.) were purchased from the indicated sources. Thiophosphoryl chloride ($PSCl_3$),[14] tetramethylbiphosphine disulfide,[12] $(CH_3)_2P(S)Br$,[15] diphenylphosphine,[16] phenylphosphine,[17] $C_6H_5P(H)CH_2CH_2PH_2$,[18,19] $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$,[20] $(CH_3)_2PCH_2CH_2PH_2$,[19]

$(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2$,[19] and $H_2PCH_2CH_2PH_2$[21] were prepared by the cited published procedures.

Preparation of Dimethylvinylphosphine Sulfide. A solution of vinylmagnesium bromide prepared from 31.2 g (1.3 mol) of magnesium turnings and 93.5 ml (139.1 g, 1.3 mol) of vinyl bromide in 650 ml of tetrahydrofuran was added through a glass wool plug into a stirred solution of 224.9 g (1.3 mol) of $(CH_3)_2P(S)Br$[15] in 800 ml of tetrahydrofuran cooled to 0°. After the addition of the vinylmagnesium bromide was completed, the tetrahydrofuran was removed at ~25° (25 mm) until a paste remained. This paste was dissolved in ~1500 ml of diethyl ether and the reaction mixture hydrolyzed with ~500 ml of deaerated water. The ether layer was separated and the aqueous layer extracted with six 50-ml portions of diethyl ether. The combined diethyl ether solutions were dried over anhydrous sodium sulfate. After filtering off the drying agent, the diethyl ether was removed from the filtrate at ~25° (25 mm). Sublimation of the solid residue at 50° (0.1 mm) gave 116.3 g (75% yield) of white crystalline dimethylvinylphosphine sulfide, $(CH_3)_2P(S)CH{=}CH_2$, mp 52–54°.

Anal. Calcd for C_4H_9PS: C, 40.0; H, 7.5; S, 26.6. Found: C, 39.9; H, 7.6; S, 26.4.

Preparation of Methyldivinylphosphine Sulfide. A stirred solution of vinylmagnesium bromide prepared from 26.4 g (1.1 mol) of magnesium turnings and 71.3 ml (107 g, 1 mol) of vinyl bromide in 1000 ml of tetrahydrofuran was treated dropwise at 0° with a solution of 75 g (0.5 mol) of $CH_3P(S)Cl_2$ in 300 ml of tetrahydrofuran. The resulting orange-red solution was then heated about 30 min to dissolve the precipitate which had separated. Tetrahydrofuran was then removed from the reaction mixture at ~25° (25 mm) until the mixture was no longer fluid. The mixture was then hydrolyzed by the successive addition of 100 ml of water followed by 700 ml of 5% aqueous sulfuric acid. The mixture was filtered to remove a considerable quantity of solid which had separated. The two liquid phases were separated from the filtrate, and the aqueous layer was washed with two 50-ml portions of diethyl ether. The combined organic layers were dried over anhydrous sodium sulfate. Removal of the drying agent by filtration followed by evaporation of the diethyl ether from the filtrate at ~25° (35 mm) gave a red-brown liquid residue. Vacuum distillation of this residue gave 18.4 g. (27% yield) of colorless liquid methyldivinylphosphine sulfide, $CH_3P(S)(CH{=}CH_2)_2$, bp 88° (0.5 mm).

Anal. Calcd for C_5H_9PS: C, 45.4; H, 6.9; S, 24.3. Found: C, 45.6; H, 6.9; S, 24.1.

Preparation of Trivinylphosphine Sulfide. A solution of 34.8 ml (56.5 g, 0.333 mol) of $PSCl_3$ in ~300 ml of tetrahydrofuran was treated at −78° with a solution of vinylmagnesium bromide prepared from 24.0 g (1 mol) of magnesium turnings and 71.8 ml (107 g, 1 mol) of vinyl bromide in ~650 ml of tetrahydrofuran. The reaction mixture was then allowed to warm to room temperature. Tetrahydrofuran was removed from the reaction mixture at ~25° (25 mm) until a pasty mass remained. This paste was treated with ~1200 ml of diethyl ether and then hydrolyzed by the subsequent addition of 500 ml of water. After removal of the insoluble material by filtration, the ether layer was removed and the aqueous layer washed with three 50-ml portions of diethyl ether. The combined diethyl ether solutions were dried over anhydrous sodium sulfate. After removal of the drying agent by filtration and the diethyl ether at 25° (25 mm), vacuum distillation of the residue gave ~2 g (~4% yield) of trivinylphosphine sulfide, bp 85° (0.35 mm).

Anal. Calcd for C_6H_9PS: C, 50.0; H, 6.3; S, 22.2. Found: C, 50.2; H, 6.4; S, 22.4.

Preparation of $(C_6H_5)_2PCH_2CH_2P(S)(CH_3)_2$. A mixture of 3.25 g (27 mmol) of dimethylvinylphosphine sulfide and 5.05 g (27 mmol) of diphenylphosphine in 75 ml of tetrahydrofuran was treated with sufficient (~0.1 g) potassium *tert*-butoxide for the reaction mixture to become warm and deep red. The resulting mixture was then boiled under reflux with stirring for 26 hr. Solvent was removed from the light red-orange reaction mixture leaving a slightly red solid. This solid was dissolved in ~125 ml of warm ethanol. Slow cooling of the ethanol solution to room temperature gave white needles which were removed by filtration, washed twice with 95% ethanol, and dried to give 7.1 g (86% yield) of $(C_6H_5)_2PCH_2CH_2P(S)(CH_3)_2$, mp 130.5°.

Anal. Calcd for $C_{16}H_{20}P_2S$: C, 62.8; H, 6.5; S, 10.4. Found: C, 62.6; H, 6.4; S, 10.5

A similar reaction on a 100-mmol scale gave 27.2 g (91% yield) of $(C_6H_5)_2PCH_2CH_2P(S)(CH_3)_2$.

Preparation of $(C_6H_5)_2PCH_2CH_2P(CH_3)_2$. A mixture of 25.1 g (82 mmol) of $(C_6H_5)_2PCH_2CH_2P(S)(CH_3)_2$, 6.2 g (16.4 mmol) of $LiAlH_4$, and 300 ml of dioxane was boiled under reflux with stirring for 19 hr. After cooling to room temperature the reaction mixture was hydrolyzed by the successive addition of 24 ml of 75% aqueous dioxane, 6 ml of 15% aqueous sodium hydroxide, and 18 ml of water. Filtration of the mixture under nitrogen in a three-necked flask with a fritted disk and stopcock at the bottom followed by vacuum distillation of the filtrate gave 18.0 g (80% yield) of colorless liquid $(C_6H_5)_2PCH_2CH_2P(CH_3)_2$, bp 160° (0.05 mm).

Anal. Calcd for $C_{16}H_{20}P_2$: C, 70.1; H, 7.3; P, 22.6. Found: C, 69.6; H, 7.5; P, 22.8.

An attempt to carry out the desulfurization of $(C_6H_5)_2PCH_2CH_2P(S)(CH_3)_2$ with $LiAlH_4$ in boiling tetrahydrofuran for 1 hr rather than in boiling dioxane as described above failed to give any $(C_6H_5)_2PCH_2CH_2P(CH_3)_2$ but instead resulted in recovery of most of the $(C_6H_5)_2PCH_2CH_2P(S)(CH_3)_2$.

Preparation of $C_6H_5P[CH_2CH_2P(S)(CH_3)_2]_2$. A mixture of 14 ml (14 g, 127 mmol) of phenylphosphine and 31.74 g (264 mmol) of dimethylvinylphosphine sulfide in 400 ml of tetrahydrofuran was treated with sufficient potassium *tert*-butoxide (three spatula tips, 0.1 g) for the tetrahydrofuran to reach the boiling point. After the exothermic reaction had subsided, the reaction mixture was treated with an additional 200 ml of tetrahydrofuran and then boiled under reflux for 13 hr with stirring. The reaction mixture was then cooled to room temperature. The resulting precipitate was filtered and dried to give 35.6 g (80% yield) of $C_6H_5P[CH_2CH_2P(S)(CH_3)_2]_2$. A second crop (6.0 g, 14% yield) was isolated from the filtrate by removal of the tetrahydrofuran at ~25° (35 mm) and crystallizing the residue from a mixture of dichloromethane and ethanol. The analytical sample, mp 162°, was obtained from such a dichloromethane–ethanol crystallization.

Anal. Calcd for $C_{14}H_{25}P_3S_2$: C, 48.0; H, 7.2; S, 18.3. Found: C, 48.1; H, 7.1; S, 18.4.

Preparation of $C_6H_5P[CH_2CH_2P(CH_3)_2]_2$. A mixture of 40.0 g (114 mmol) of $C_6H_5P[CH_2CH_2P(S)(CH_3)_2]_2$, 17.5 g (456 mmol) of $LiAlH_4$, and 1000 ml of dioxane in a 2-l. flask was boiled under reflux with stirring for 20 hr. After cooling to room temperature the reaction mixture was hydrolyzed by the successive addition of 70 ml of 75% aqueous dioxane, 17.5 ml of 15% aqueous sodium hydroxide, and 52 ml of water. Vacuum distillation of the resulting liquid gave 25.3 g (80% yield) of colorless liquid $C_6H_5P[CH_2CH_2P(CH_3)_2]_2$, bp 147° (0.08 mm).

Anal. Calcd for $C_{14}H_{25}P_3$: C, 58.7; H, 8.8; P, 32.5. Found: C, 59.1; H, 9.0; P, 31.4.

Preparation of $CH_3P(S)[CH_2CH_2P(C_6H_5)_2]_2$. A mixture of 3.87 g (29 mmol) of methyldivinylphosphine sulfide and 12.7 g (68 mmol) of diphenylphosphine in 150 ml of tetrahydrofuran was treated with several spatula tips (~0.1 g) of potassium *tert*-butoxide until a yellow color persisted. The reaction mixture was boiled under reflux with stirring for 16 hr. Solvent was then removed at 25° (25 mm). Crystallization of the residue from 350 ml of boiling absolute ethanol gave 13.2 g (95% yield) of white crystalline $CH_3P(S)[CH_2CH_2P(C_6H_5)_2]_2$. The analytical sample, mp 130–131°, was purified by further recrystallization from hot ethanol (40 ml/g).

Anal. Calcd for $C_{29}H_{31}P_3S$: C, 69.0; H, 6.2; S, 6.4. Found: C, 68.8; H, 6.2; S, 6.2.

Preparation of $CH_3P[CH_2CH_2P(C_6H_5)_2]_2$. (a) By Desulfurization of $CH_3P(S)[CH_2CH_2P(C_6H_5)_2]_2$. A mixture of 12.3 g (24.4 mmol) of $CH_3P(S)[CH_2CH_2P(C_6H_5)_2]_2$, 2.3 g (60.5 mmol) of $LiAlH_4$, and 300 ml of dioxane was boiled under reflux for 18 hr. After cooling to room temperature the reaction mixture was hydrolyzed by the successive addition of 10 ml of 75% aqueous dioxane, 2.5 ml of 15% aqueous sodium hydroxide, and 7.5 ml of water. The hydrolyzed mixture was filtered in the fritted three-necked flask and dioxane was removed from the filtrate at ~10 mm. The proton nmr spectrum of the solid residue after one crystallization from deaerated hot absolute ethanol indicated incomplete desulfurization. Therefore this crude product was boiled under reflux with an additional 4.0 g (105 mmol) of $LiAlH_4$ in 100 ml of dioxane for 19 hr with stirring. Hydrolysis of the resulting mixture by a similar process (with proportionately increased quantities of water and sodium hydroxide) followed by solvent removal and crystallization from 200 ml of hot deaerated absolute ethanol gave 6.6 g (57% yield) of white needles of $CH_3P[CH_2CH_2P(C_6H_5)_2]_2$, mp 72–74°.

Anal. Calcd for $C_{29}H_{31}P_3$: C, 73.7; H, 6.6; P, 19.7; mol wt, 472. Found: C, 73.8; H. 6.6; P, 20.2; mol wt, 474 (benzene).

(b) By Reaction of CH_3PH_2 with $(C_6H_5)_2PCH{=}CH_2$. Methylphosphine, generated by addition of a solution of 8.6 ml (9.92 g, 80 mmol) of dimethyl methylphosphonate in 50 ml of dioxane to 5.0 g (132 mmol) of $LiAlH_4$ in 150 ml of dioxane, was bubbled under the surface of a boiling solution of 14.0 g (66 mmol) of freshly vacuum distilled diphenylvinylphosphine in 200 ml of tetrahydrofuran containing sufficient potassium *tert*-butoxide (four spatula tips, ~0.1g) to produce a persistent pale yellow color. A −78° reflux condenser was attached to the reaction flask to prevent escape of the methylphosphine. After the addition of the methylphosphine was complete, the reaction mixture was boiled under reflux with stirring for 18 hr using the −78° reflux condenser for the first 6 hr. Solvent was then removed from the reaction mixture at ~25° (25 mm). Vacuum distillation of the liquid residue gave 6.8 g (49% recovery) of unreacted diphenylvinylphosphine. The residue from the vacuum distillation crystallized upon standing for 24 hr at room temperature. The resulting solid was washed with ~15 ml of deaerated ethanol and dried to give 3.0 g (19% conversion, 37% yield) of white $CH_3P[CH_2CH_2P(C_6H_5)_2]_2$, mp 71–72°, identified by comparison of its proton nmr spectrum with that of material prepared by desulfurization of $CH_3P(S)[CH_2CH_2P(C_6H_5)_2]_2$ as described above.

Preparation of $CH_3P[CH_2CH_2P(S)(CH_3)_2]_2$. Methylphosphine, generated by the dropwise addition of a solution of 21.6 ml (24.8 g, 200 mmol) of dimethyl methylphosphonate in 50 ml of dioxane to 11.0 g (290 mmol) of $LiAlH_4$ in 200 ml of dioxane, was passed into a flask containing 1.0 g (8.9 mmol) of potassium *tert*-butoxide in 400 ml of tetrahydrofuran boiling under reflux. After about one-fourth of the methylphosphine had been added, a solution of 25 g (200 mmol) of dimethylvinylphosphine sulfide in 200 ml of tetrahydrofuran was added dropwise to the potassium *tert*-butoxide solution while continuing the generation of the methylphosphine. A −78° reflux condenser was used to prevent escape of the methylphosphine. The dimethylvinylphosphine sulfide solution was added at a rate relative to the generation of the methylphosphine such that refluxing methylphosphine was always observed. This prevented destruction of the dimethylvinylphosphine sulfide by the catalyst before it could react with the methylphosphine. The addition of the dimethylvinylphosphine sulfide took 2 hr. After the addition of the dimethylvinylphosphine sulfide was complete, the reaction mixture was boiled under reflux for 28 hr using the −78° condenser for the first 4 hr of this heating period. At this point the solution was slate blue and contained a large quantity of precipitated solid. Tetrahydrofuran was then removed at 40° (40 mm). The resulting brownish solid was boiled with 400 ml of deaerated ethanol. Filtration of the ethanol-insoluble material gave 22.0 g (76% yield) of crude $CH_3P[CH_2CH_2P(S)(CH_3)_2]_2$ as a brownish solid. The analytical sample, mp 83–84°, was purified further by successive low temperature crystallizations first from a mixture of dichloromethane and hexane and then from ethanol.

Anal. Calcd for $C_9H_{23}P_3S_2$: C, 37.5; H, 8.0; S, 22.2. Found: C, 37.4; H, 8.0; S, 22.4.

Preparation of $CH_3P(S)[CH_2CH_2P(CH_3)_2]_2$. Dimethylphosphine was generated by heating a mixture of 27.9 g (150 mmol) of tetramethylbiphosphine sulfide, 8.5 g (224 mmol) of $LiAlH_4$, and 250 ml of dioxane to 80–100° and distilled through a 30-cm Vigreux column into a reaction flask containing a solution of 14.0 g (106 mmol) of $CH_3P(S)(CH{=}CH_2)_2$ in 200 ml of tetrahydrofuran and cooled to −78°. Escape of the dimethylphosphine was prevented by −78° condensers. After all of the dimethylphosphine had been collected in the reaction flask, the resulting mixture in the reaction flask was treated with a solution of 0.2 g of potassium *tert*-butoxide in 50 ml of tetrahydrofuran. The reaction mixture was boiled under reflux for 30 hr using a −78° reflux condenser during the first hour of heating. The reaction mixture was then stirred for an additional 24 hr at room temperature while sweeping out any unreacted dimethylphosphine in a stream of nitrogen. Tetrahydrofuran was then removed from the reaction mixture at 0.1 mm. Since this tetrahydrofuran still had a dimethylphosphine odor, it was collected in a −78° trap and discarded by treatment with aqueous calcium hypochlorite. The solid remaining in the reaction flask was crystallized from warm deaerated ethanol to give 13.8 g (51% yield) of $CH_3P(S)[CH_2CH_2P(CH_3)_2]_2$. The analytical sample, mp 83–84°, was purified further by successive low temperature crystallizations first from a mixture of dichloromethane and hexane and then from ethanol.

Anal. Calcd for $C_9H_{23}P_3S$: C, 42.2; H, 9.0; S, 12.5. Found: C, 42.3; H, 9.1; S, 12.6.

Preparation of $CH_3P[CH_2CH_2P(CH_3)_2]_2$. (a) From Desulfurization of $CH_3P[CH_2CH_2P(S)(CH_3)_2]_2$. A mixture of 12.0 g (42 mmol) of $CH_3P[CH_2CH_2P(S)(CH_3)_2]_2$, 3.0 g (79 mmol) of $LiAlH_4$, and 150 ml of dioxane was boiled under reflux with stirring for 24 hr. After standing at room temperature for 48 hr the reaction mixture was hydrolyzed by the successive addition of 12 ml of 75% aqueous dioxane, 3 ml of 15% aqueous sodium hydroxide, and 9 ml of water. Removal of solvent after filtration gave a liquid containing a considerable amount of solid and exhibiting $-P(S)(CH_3)_2$ as well as $-P(CH_3)_2$ methyl resonances in the proton nmr spectrum. This mixture was therefore reduced again with an additional 3.0 g (79 mmol) of $LiAlH_4$ in 100 ml of boiling dioxane for 16 hr. Hydrolysis as before followed by vacuum distillation gave 5.1 g (55% yield) of colorless liquid $CH_3P[CH_2CH_2P(CH_3)_2]_2$, bp 95° (0.15 mm), identified by comparison of its proton nmr spectrum with that of the product obtained by desulfurization of $CH_3P(S)[CH_2CH_2P(CH_3)_2]_2$ as described below.

(b) From Desulfurization of $CH_3P(S)[CH_2CH_2P(CH_3)_2]_2$. A mixture of 27.1 g (106 mmol) of $CH_3P(S)[CH_2CH_2P(CH_3)_2]_2$, 6.0 g (158 mmol) of $LiAlH_4$, and 125 ml of dioxane was boiled under reflux with stirring for 22 hr. After cooling to room temperature, the reaction mixture was hydrolyzed by the successive addition of 6 ml of water, 6 ml of 15% aqueous sodium hydroxide, and 18 ml of water. The filtered solution was distilled under vacuum to give after removal of the dioxane 12.1 g (51% yield) of colorless liquid $CH_3P[CH_2CH_2P(CH_3)_2]_2$, bp 103° (0.3 mm). The distillate solidified upon standing in the freezer at −10°.

Anal. Calcd for $C_9H_{23}P_3$: C, 48.2; H, 10.3; P, 41.4. Found: C, 48.4; H, 10.6; P, 41.3.

Preparation of $(CH_3)_2P(S)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(S)(CH_3)_2$. A solution of 12.2 g (50 mmol) of $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ and 12.0 g (100 mmol) of dimethylvinylphosphine sulfide in 250 ml of tetrahydrofuran was treated with sufficient solid potassium *tert*-butoxide (about four spatula tips, ~0.1 g)) to give a deep yellow color which became deep red over 2–3 min. The resulting mixture was boiled under reflux with stirring for 16 hr. Solvent was removed from the black reaction mixture at ~25° (25 mm). The residue was boiled under reflux with 200 ml of ethanol. The slurry was cooled to room temperature and filtered to give 23.5 g (97% yield) of crude $(CH_3)_2P(S)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(S)(CH_3)_2$. The analytical sample, mp 160–162°, was purified by crystallization from a mixture of dichloromethane and ethanol.

Anal. Calcd for $C_{22}H_{34}P_4S_2$: C, 54.3; H, 7.0; S, 13.2. Found: C, 54.0; H, 7.0; S, 13.4.

Preparation of the Linear Tetra(tertiary phosphine) $(CH_3)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(CH_3)_2$. A mixture of 20.0 g (41 mmol) of $(CH_3)_2P(S)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(S)(CH_3)_2$, 4.0 g (105 mmol) of $LiAlH_4$, and 100 ml of dioxane was boiled under reflux for 22 hr with stirring. Hydrolysis of the reaction mixture by the successive additions of 4 ml of water, 4 ml of 15% aqueous sodium hydroxide, and 12 ml of water followed by removal of the dioxane from the filtered reaction mixture at ~10 mm gave an oily residue which solidified upon standing. Crystallization of this solid from ~150 ml of deaerated ethanol gave 13.0 g of a white solid. The proton nmr spectrum of this solid showed both $-P(CH_3)_2$ and $-P(S)(CH_3)_2$ resonances indicating that the desulfurization was incomplete. This product was therefore boiled under reflux with stirring with 3.0 g (79 mmol) of $LiAlH_4$ in 200 ml of dioxane for 16 hr. Hydrolysis by the successive addition of 3 ml of water, 3 ml of 15% aqueous sodium hydroxide, and 9 ml of water followed by removal of solvent from the filtrate gave a white solid which after crystallization from 50 ml of deaerated ethanol gave 5.0 g (29% yield) of white $(CH_3)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(CH_3)_2$, mp 73–74°.

Anal. Calcd for $C_{24}H_{34}P_4$: C, 62.5; H, 8.1; P, 29.4; mol wt, 422. Found: C, 62.6; H, 8.5; P, 29.0; mol wt 429 (benzene).

Preparation of $[(CH_3)_2P(S)CH_2CH_2]_2PCH_2CH_2P(CH_3)_2$. A mixture of 10.71 g (89.5 mmol) of $(CH_3)_2PCH_2CH_2PH_2$[19] and 21.4 g (179 mmol) of dimethylvinylphosphine sulfide in 200 ml of tetrahydrofuran was treated with ~0.1 g of potassium *tert*-butoxide. After the resulting exothermic reaction had subsided, the reaction mixture was heated to the boiling point until so much solid formed that the reaction mixture became immobile. The tetrahydrofuran was then removed at ~25° (25 mm). The residue was washed with 300 ml of deaerated ethanol to give 30.0 g (93% yield) of white very fluffy $[(CH_3)_2P(S)CH_2CH_2]_2PCH_2CH_2P(CH_3)_2$, mp 320–325°.

Anal. Calcd for $C_{12}H_{30}P_4S_2$: C, 39.8; H, 8.3; S, 17.7. Found: C, 39.9; H, 8.4; S, 17.8.

Preparation of the Tripod Tetra(tertiary phosphine) $P[CH_2CH_2P(CH_3)_2]_3$. (a) From Trivinylphosphine Sulfide. Dimethylphosphine, generated from 27.9 g (150 mmol) of tetramethylbiphosphine disulfide and 5.7 g (150 mmol) of $LiAlH_4$ in dioxane by a procedure similar to that used in the preparation of $CH_3P(S)[CH_2CH_2P(CH_3)_2]_2$ described above, was collected in a reaction flask containing 10.1 g (70 mmol) of crude trivinylphosphine sulfide and 250 ml of tetrahydrofuran cooled to −78°. Potassium *tert*-butoxide (~0.1 g) was added and the reaction mixture was allowed to warm to room temperature and then boiled under reflux for 1 hr using a −78° condenser to prevent escape of the dimethylphosphine. After boiling under reflux for an additional 13 hr with a water-cooled reflux condenser, solvent was removed from the dark reaction mixture at ~10 mm trapping the solvent in a −78° bath and decomposing the collected solvent with aqueous calcium hypochlorite to prevent escape of the dimethylphosphine. The crude product, exhibiting a proton nmr spectrum consistent with the presence of the expected adduct $SP[CH_2CH_2P(CH_3)_2]_3$, was boiled under reflux with 3.0 g (79 mmol) of $LiAlH_4$ in 100 ml of dioxane for 32 hr. The solution was then hydrolyzed by the successive addition with cooling of 3 ml of water, 3 ml of 15% aqueous sodium hydroxide, and 9 ml of water. Distillation of the filtered reaction mixture gave after removal of the dioxane 1.67 g (8% yield) of slightly yellow liquid $P[CH_2CH_2P(CH_3)_2]_3$, bp ~125° (0.35 mm), which solidified in a freezer at −10°. The analytical sample was purified by two sublimations at 110° (0.3 mm) onto a −78° probe.

Anal. Calcd for $C_{12}H_{30}P_4$: C, 48.3; H, 10.1; P, 41.5; mol wt, 298. Found: C, 48.4; H, 10.0; P, 41.0; mol wt, 307 (benzene).

(b) By Desulfurization of $[(CH_3)_2P(S)CH_2CH_2]_2PCH_2CH_2P(CH_3)_2$. A mixture of 29.0 g (80 mmol) of $[(CH_3)_2P(S)CH_2CH_2]_2PCH_2CH_2P(CH_3)_2$, 5.0 g (132 mmol) of $LiAlH_4$, and 500 ml of dioxane was boiled under reflux for 24 hr with stirring. An additional 1.0 g (26 mmol) of $LiAlH_4$ was added after 16 hr of the heating. The reaction mixture was hydrolyzed by the successive addition of 6 ml of water, 6 ml of 15% aqueous sodium hydroxide, and 18 ml of water. Filtration followed by distillation of the liquid gave after removal of the dioxane 16.0 g (67% yield) of liquid $P[CH_2CH_2P(CH_3)_2]_3$, bp 130° (0.3 mm), mp 45–46°.

Anal. Calcd for $C_{12}H_{30}P_4$: C, 48.3; H, 10.1; P, 41.5. Found: C, 48.2; H, 10.2; P, 41.4.

Preparation of $P[CH_2CH_2P(S)(CH_3)_2]_3$. Phosphine, generated by addition of 67% aqueous dioxane to a dioxane slurry of 8.7 g (150 mmol) of aluminum phosphide, was passed into a solution of 0.5 g (4.5 mmol) of potassium *tert*-butoxide in 600 ml of tetrahydrofuran. As soon as the system was saturated with phosphine, dropwise addition of a solution of 19.0 g (158 mmol) of dimethylvinylphosphine sulfide in 150 ml of tetrahydrofuran was begun while the generation of phosphine was continued. The rate of addition of the dimethylvinylphosphine sulfide relative to the rate of phosphine generation was adjusted so that the reaction mixture did not become orange. If the reaction mixture became orange, addition of the dimethylvinylphosphine sulfide was suspended until the orange color had been discharged by the phosphine being generated. During the course of this reaction a flocculent white precipitate formed. To avoid loss of the phosphine before it could react, the use of a nitrogen stream was avoided after the air had been displaced at the beginning and sufficient phosphine had been generated to fill the system. After the generation of the phosphine and the addition of the dimethylvinylphosphine sulfide were both complete, excess phosphine was displaced by reintroduction of the nitrogen stream. Tetrahydrofuran was then removed at ~25° (35 mm). The white solid residue was boiled with 450 ml of deaerated ethanol and then collected on a filter under nitrogen to give 19.0 g (91% yield) of white insoluble $P[CH_2CH_2P(S)(CH_3)_2]_3$, mp ~360°.

Anal. Calcd for $C_{12}H_{30}P_4S_3$: C, 36.6; H, 7.6; S, 24.4. Found: C, 36.4; H, 7.7; S, 24.6.

Conversion of $P[CH_2CH_2P(S)(CH_3)_2]_3$ to $HP[CH_2CH_2P(CH_3)_2]_2$. A mixture of 7.8 g (20 mmol) of $P[CH_2CH_2P(S)(CH_3)_2]_3$, 2.0 g (53 mmol) of $LiAlH_4$, and 100 ml of dioxane was boiled under reflux with stirring for 90 hr with introduction of additional 1.0 g (26 mmol each) portions of $LiAlH_4$ after 5 and 17 hr of this heating. The reaction mixture was then cooled to room temperature and treated with sufficient diethyl ether to make it mobile. The mixture was then hydrolyzed by the successive addition of 4 ml of water, 4 ml of 15% aqueous sodium hydroxide, and 12 ml of water. Filtration followed by solvent removal and vacuum distillation in a short path apparatus gave 1.5 g (26%) yield) of liquid $HP[CH_2CH_2P(CH_3)_2]_2$, bp 85° (0.1 mm). This liquid was spontaneously flammable in air when absorbed on tissue paper.

Anal. Calcd for $C_8H_{21}P_3$: C, 45.7; H, 10.0; P, 44.2; mol wt, 210. Found: C, 45.9; H, 9.9; P, 43.9; mol wt, 218 (benzene).

Infrared Spectrum (liquid film): ν(CH) bands at 2962 (s), 2953 (s), 2928 (m), 2894 (s), and 2811 (m) cm^{-1}; ν(PH) band at 2270 (m) cm^{-1}; other bands at 1427 (s), 1419 (s), 1288 (m), 1272 (w), 1168 (w), 1099 (w), 1017 (vw), 958 (vw), 935 (s), 889 (m), 858 (w), 811 (w), and 702 (s) cm^{-1}.

Preparation of the Penta(tertiary phosphine) Trisulfide. A mixture of 6.8 g (40 mmol) of $C_6H_5P(H)CH_2CH_2PH_2$, 14.4 g (120 mmol) of dimethylvinylphosphine sulfide, ~0.1 g (three spatula tips) of potassium *tert*-butoxide, and 200 ml of tetrahydrofuran was boiled under reflux with stirring for 12 hr. A voluminous white solid separated. Tetrahydrofuran was removed at ~25° (25 mm). The white solid was washed with 200 ml of boiling deaerated absolute ethanol and dried to give 20 g (94% yield of $(CH_3)_2P(S)CH_2CH_2P(C_6H_5)CH_2CH_2P[CH_2CH_2P(S)(CH_3)_2]_2$, mp 195–200°, soluble in hot dioxane and in cold dichloromethane.

Anal. Calcd for $C_{20}H_{39}P_5S_3$: C, 45.3; H, 7.4; S, 18.1. Found: C, 45.2; H, 7.5; S, 18.3.

Preparation of the Penta(tertiary phosphine) $(CH_3)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P[CH_2CH_2P(CH_3)_2]_2$. A mixture of 19.5 g (37 mmol) of the penta(tertiary phosphine) trisulfide described above, 3.0 g (79 mmol) of $LiAlH_4$, and 100 ml of dioxane was boiled under reflux for 17 hr. After cooling to room temperature the reaction mixture was hydrolyzed by the successive addition of 3 ml of water, 3 ml of 15% aqueous sodium hydroxide, and 9 ml of water. The reaction mixture was filtered and solvent removed from the filtrate at ~10 mm. Vacuum distillation of the liquid residue gave 11.3 g (71% yield) of the liquid penta (tertiary phosphine) $(CH_3)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P[CH_2CH_2P(CH_3)_2]_2$, bp 220–225° (0.2–0.4 mm).

Anal. Calcd for $C_{20}H_{39}P_5$: C, 55.3; H, 9.0; P, 35.7; mol wt, 434. Found: C, 55.2; H, 9.2; P, 35.7; mol wt, 419 (benzene).

Preparation of the Hexa(tertiary phosphine) Tetrasulfide. A mixture of 4.27 g (45 mmol) of $H_2PCH_2CH_2PH_2$ and 21.6 g (180 mmol) of dimethylvinylphosphine sulfide in 250 ml of tetrahydrofuran was treated with ~0.1 g (four spatula tips) of potassium *tert*-butoxide. The reaction mixture was then boiled for 5 hr under reflux with stirring. A large quantity of white solid separated during this reaction. After the reaction was completed, tetrahydrofuran was removed at ~25° (25 mm). The residue was washed with ~250 ml of deaerated ethanol and dried to give 25.3 g 100% yield) of the hexa(tertiary phosphine) tetrasulfide $[(CH_3)_2P(S)CH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(S)(CH_3)_2]_2$, mp 224–225°.

Anal. Calcd for $C_{18}H_{44}P_6S_4$: C, 37.6; H, 7.7; S, 22.3. Found: C, 37.8; H, 7.8; S, 22.3.

Attempts to reduce this hexa(tertiary phosphine) tetrasulfide with excess $LiAlH_4$ in boiling dioxane to give the corresponding hexa(tertiary phosphine) were unsuccessful.

Preparation of the Hexa(tertiary phosphine) Trisulfide. A mixture of 8.92 g (49 mmol) of the tertiary-secondary-primary triphosphine[19] $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2$ and 17.7 g (148 mmol) of dimethylvinylphosphine sulfide in 250 ml of tetrahydrofuran was treated with sufficient potassium *tert*-butoxide (one spatula tip, ~0.05 g) to cause the mixture to turn red and become warm. The reaction proceeded without external heating to give a white pasty reaction mixture. After the reaction was complete, tetrahydrofuran was removed at ~25° (25 mm). The solid residue was washed with ethanol until the washings were colorless and then dried at ~25° (0.1 mm) for 48 hr to give 26 g (98% yield) of the white very fluffy hexa(tertiary phosphine) trisulfide $[(CH_3)_2PCH_2CH_2][(CH_3)_2P(S)CH_2CH_2]PCH_2CH_2P[CH_2CH_2P(S)(CH_3)_2]_2$, mp 177–179°.

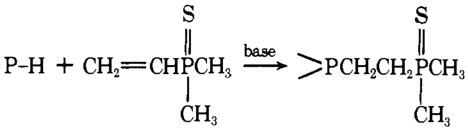
Anal. Calcd for $C_{18}H_{44}P_6S_3$: C, 39.8; H, 8.1; S, 17.7. Found: C, 39.9; H, 7.9; S, 17.8.

Preparation of the Hexa(tertiary phosphine) $[(CH_3)_2PCH_2CH]_2PCH_2CH_2P[CH_2CH_2P(CH_3)_2]_2$. A mixture of 26.0 g (48 mmol) of the hexa(tertiary phosphine) trisulfide described above, 5.0 g (132 mmol) of $LiAlH_4$, and 400 ml of dioxane was boiled under reflux with stirring for 24 hr. After cooling to room temperature, the reaction mixture was hydrolyzed by the successive addition of 5 ml of water, 5 ml of 15% aqueous sodium hydroxide, and 15 ml of water. The reaction mixture was filtered and solvent was removed from the filtrate at ~10 mm. Distillation of the partially solidified residue gave a total of 15.2 g (71% yield) of the hexa(tertiary phosphine) $[(CH_3)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(CH_3)_2]_2$, bp 200–201° (0.02 mm), which partially solidified on standing at room temperature.

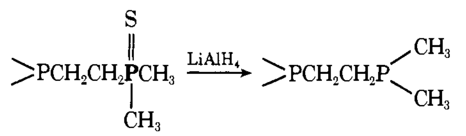
Anal. Calcd for $C_{18}H_{44}P_6$: C, 48.5; H, 9.9; P, 41.6; mol wt, 446. Found: C, 48.4; H, 10.2; P, 41.5; mol wt, 430 (benzene).

Discussion

Most of the syntheses of methylated poly(tertiary phosphines) discussed in this paper employ the conversion of a P-H bond to a $PCH_2CH_2P(CH_3)_2$ unit by the two-step procedure shown in eq 1 and 2. The first step is a base-catalyzed Michael addition[22] similar to the previously reported base-catalyzed additions of phosphorus-hydrogen bonds to the vinyl double bonds in vinylphosphines[4] and vinylphosphonates.[18] In all cases the first step of the synthetic sequence was performed in boiling tetrahydrofuran with potassium *tert*-butoxide as the base catalyst, since these conditions were found to be most effective in our earlier work.[18] The second step involves desulfurization of the phosphine-phosphine sulfide adduct and was performed in boiling dioxane using $LiAlH_4$. An attempt to carry out the desulfurization of $(CH_3)_2P(S)CH_2CH_2P(C_6H_5)_2$ with $LiAlH_4$ in boiling tetrahydrofuran rather than boiling dioxane failed presumably because the lower boiling point of the tetrahydrofuran is insufficient for the reaction.

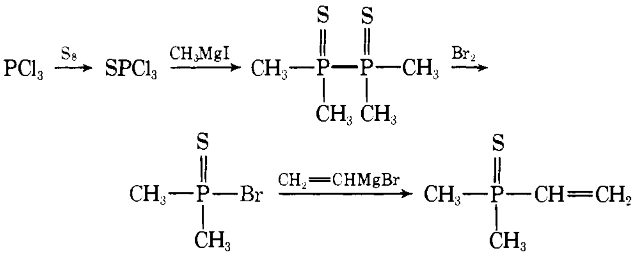


$$\text{P-H} + CH_2{=}CH\underset{CH_3}{\overset{S}{P}}CH_3 \xrightarrow{\text{base}} {>}PCH_2CH_2\underset{CH_3}{\overset{S}{P}}CH_3 \qquad (1)$$



(2)

This work required large quantities of dimethylvinylphosphine sulfide which could be obtained by the following four-step sequence starting with inexpensive materials.



$$PCl_3 \xrightarrow{S_8} SPCl_3 \xrightarrow{CH_3MgI} CH_3-\underset{CH_3}{\overset{S}{P}}-\underset{CH_3}{\overset{S}{P}}-CH_3 \xrightarrow{Br_2} CH_3-\underset{CH_3}{\overset{S}{P}}-Br \xrightarrow{CH_2{=}CHMgBr} CH_3-\underset{CH_3}{\overset{S}{P}}-CH{=}CH_2$$

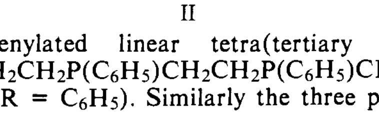
The first three steps of the above sequence are well-established procedures, but the final step has not been previously reported. Dimethylvinylphosphine sulfide is a white solid which can be readily purified on a large scale by vacuum sublimation. It fumes with a white vapor upon exposure to air, and upon prolonged exposure to air it becomes liquid. For this reason dimethylvinylphosphine sulfide and the other vinylphosphine sulfides were always protected by storage under dry nitrogen in the dark.

Similar reaction sequences could be used to obtain methyldivinylphosphine sulfide and trivinylphosphine sulfide, but the yields in the final steps involving reactions with vinylmagnesium bromide decrease drastically as the number of vinyl groups bonded to the phosphorus atom is increased.

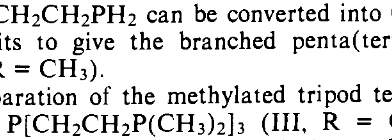
The simplest illustration of the above two-step conversion of a P-H bond to a $PCH_2CH_2P(CH_3)_2$ unit using dimethylvinylphosphine sulfide is the conversion of diphenylphosphine to the di(tertiary phosphine) $(C_6H_5)_2PCH_2CH_2P(CH_3)_2$. This compound complements the extensive series of mixed alkyl-aryl di(tertiary phosphines) prepared by Grim and coworkers.[23]

Variations of this method have been used to prepare three different tri(tertiary phosphines) of the general type $R'P(CH_2CH_2PR_2)_2$ ($R' = CH_3$, $R = CH_3$ or C_6H_5; $R' = C_6H_5$, $R = CH_3$). Thus the compound $C_6H_5P[CH_2CH_2P(CH_3)_2]_2$ can be prepared by the conversion of both P-H bonds in $C_6H_5PH_2$ into $CH_2CH_2P(CH_3)_2$ units by the two-step sequence discussed above. The compound $CH_3P[CH_2CH_2P(C_6H_5)_2]_2$ can be obtained by addition of 2 equiv of $(C_6H_5)_2PH$ to the vinyl double bonds in methyldivinylphosphine sulfide followed by $LiAlH_4$ desulfurization. However, $CH_3P[CH_2CH_2P(C_6H_5)_2]_2$ can also be obtained as least as easily by the base-catalyzed addition of both phosphorus-hydrogen bonds in methylphosphine to the vinyl double bonds in 2 equiv of diphenylvinylphosphine without involving any phosphine sulfide intermediates, since, as indicated above, the yield in the vinylation of $CH_3P(S)Cl_2$ to methyldivinylphosphine sulfide is rather low. The completely aliphatic tri(tertiary phosphine) $CH_3P[CH_2CH_2P(CH_3)_2]_2$ can be prepared by two methods involving vinylphosphine sulfides starting with either $(CH_3)_2PH$ and $CH_3P(S)(CH{=}CH_2)_2$ in a 2:1 mole ratio or with CH_3PH_2 and $(CH_3)_2P(S)CH{=}CH_2$ in a 1:2 mole ratio followed by the usual $LiAlH_4$ desulfurization in either case.

The two phosphorus-hydrogen bonds in the di(secondary phosphine) $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ can be converted into $CH_2CH_2P(CH_3)_2$ units by using dimethylvinylphosphine sulfide according to the general two-step reaction sequence to give the mixed aliphatic-aromatic linear tetra(tertiary phosphine) $(CH_3)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(CH_3)_2$ (I, $R = CH_3$) similar to the reported[4] phenylated linear tetra(tertiary phosphine) $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (I, $R = C_6H_5$). Similarly the three phosphorus-hydrogen bonds in the secondary-primary diphosphine $C_6H_5P(H)CH_2CH_2PH_2$ can be converted into $CH_2CH_2P(CH_3)_2$ units to give the branched penta(tertiary phosphine) II ($R = CH_3$).

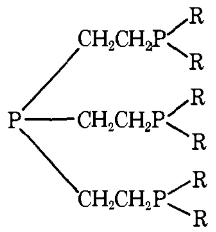


I



II

The preparation of the methylated tripod tetra(tertiary phosphine) $P[CH_2CH_2P(CH_3)_2]_3$ (III, $R = CH_3$) illustrates some difficulties associated with the synthetic procedures described in this paper. The tripod tetra(tertiary phosphine) III ($R = CH_3$) was first prepared by the base-



III

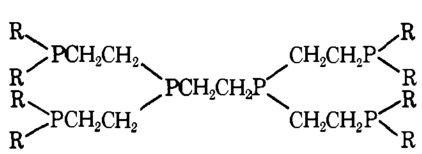
catalyzed addition of 3 equiv of dimethylphosphine to trivinylphosphine sulfide followed by $LiAlH_4$ desulfurization. This method yielded sufficient $P[CH_2CH_2P(CH_3)_2]_3$ (III, R = CH_3) for characterization by elemental analyses and nmr but insufficient material for the study of the coordination chemistry of this interesting ligand, since trivinylphosphine sulfide could only be obtained in low and erratic yields by any of the reactions that were tried ($PSCl_3$ + vinylmagnesium bromide, $PSCl_3$ + vinyllithium, and $PSBr_3$ + vinylmagnesium bromide at various temperatures).

In order to circumvent these difficulties the addition of the three phosphorus-hydrogen bonds of phosphine to 3 equiv of dimethylvinylphosphine sulfide was next investigated. This gave the expected adduct $P[CH_2CH_2P(S)(CH_3)_2]_3$ provided that the reaction conditions during the base-catalyzed addition were controlled so that excess phosphine over dimethylvinylphosphine sulfide was always present. However, the solubility of this adduct in boiling dioxane was so low that desulfurization with $LiAlH_4$ did not occur under the conditions successful for the other phosphine-phosphine sulfides. If the reaction between $P[CH_2CH_2P(S)(CH_3)_2]_3$ and excess $LiAlH_4$ in boiling dioxane was carried out under forcing conditions using an exceptionally long 90-hr reaction period, hydrogenolysis of one of the carbon-phosphorus bonds occurred giving the novel di(tertiary)-secondary phosphine) $HP[CH_2CH_2P(CH_3)_2]_2$ in 26% yield. The P-H bond in $HP[CH_2CH_2P(CH_3)_2]_2$ was indicated by the 2270-cm^{-1} ν(PH) frequency in the infrared spectrum and by a doublet ($J \approx 193$ Hz) at 56.7 ppm in the phosphorus-31 nmr spectrum.

The difficulty in desulfurizing $P[CH_2CH_2P(S)(CH_3)_2]_3$ with $LiAlH_4$ in boiling dioxane indicates that a certain minimum solubility of the phosphine-phosphine sulfide in boiling dioxane is necessary before the desulfurization can be performed successfully. Furthermore, our observations indicate that the solubilities of phosphine-phosphine sulfides in organic solvents decrease as the ratio of phosphine sulfide units to phosphine units is increased.

These considerations suggested that the successful synthesis of the tripod tetra(tertiary phosphine) $P[CH_2CH_2P(CH_3)_2]_3$ (III, R = CH_3) in quantity using the methods described in this paper would require a phosphine-phosphine sulfide with a lower ratio of phosphine sulfide units to phosphine units than $P[CH_2CH_2P(S)(CH_3)_2]_3$. Accordingly, the tertiary-primary diphosphine[19] $(CH_3)_2PCH_2CH_2PH_2$ was added to 2 equiv of dimethylvinylphosphine sulfide to give the expected adduct $(CH_3)_2PCH_2CH_2P[CH_2CH_2P(S)(CH_3)_2]_2$, which gave the desired tripod tetra(tertiary phosphine) $P[CH_2CH_2P(CH_3)_2]_3$ (III, R = CH_3) in 67% yield upon $LiAlH_4$ desulfurization. Pure tripod tetra(tertiary phosphine) III (R = CH_3), unlike the other methylated poly(tertiary phosphines) not containing phenyl groups, is crystalline at room temperature.

The phenylated hexa(tertiary phosphine) IV (R = C_6H_5) has been prepared[4] by adding 4 equiv of diphenylvinylphosphine to the phosphorus-hydrogen bonds of the di(primary phosphine) $H_2PCH_2CH_2PH_2$. An analogous attempt to convert the four phosphorus-hydrogen bonds in $H_2PCH_2CH_2PH_2$ into $CH_2CH_2P(CH_3)_2$ units by addition to 4 equiv of dimethylvinylphosphine sulfide followed by $LiAlH_4$ desulfurization to give the methylated hexa(tertiary phosphine) IV (R = CH_3) failed owing to insufficient solubility of the intermediate hexa(tertiary phosphine) tetrasulfide adduct $[(CH_3)_2P(S)CH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(S)(CH_3)_2]_2$ similar to the difficulties in the preparation of the tripod tetra(tertiary phosphine) III (R = CH_3) by desulfurization of $P[CH_2CH_2P(S)(CH_3)_2]_3$. These difficulties could be circumvented by using the $LiAlH_4$ desulfurization of the hexa(tertiary phosphine) trisulfide obtained by addition of the tertiary-secondary-primary triphosphine $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2$ to 3 equiv of dimethylvinylphosphine sulfide for the preparation of the methylated hexa(tertiary phosphine) IV (R = CH_3).



IV

The new methylated poly(tertiary phosphines) can be characterized by their proton (Table I) and phosphorus-31 (Table II) nmr spectra in addition to their elemental analyses. The proton nmr spectra are useful for indicating the completeness of the $LiAlH_4$ desulfurizations, since the methyl protons of $(CH_3)_2P(S)CH_2CH_2$- units exhibit doublets in the range τ 8.3-8.5 with coupling constants of 12-13 Hz whereas the methyl protons of the desulfurized $(CH_3)_2PCH_2CH_2$- units exhibit doublets in the range τ 9.0-9.3 with the much smaller coupling constants of 2-3 Hz. The broad resonances from the protons of CH_2CH_2 bridges bonded to $(CH_3)_2P$ units fall in the range τ 8.55-8.75 which is distinctly higher than the range τ 8.0-8.2 found for CH_2CH_2 bridges bonded to $(C_6H_5)_2P$ units.

Some curious effects were observed in the multiplicity of the methyl proton resonances in the poly(tertiary phosphines) containing $(CH_3)_2P$ groups. The $(CH_3)_2P$ proton resonances in $(C_6H_5)_2PCH_2CH_2P(CH_3)_2$, $CH_3P[CH_2CH_2P(CH_3)_2]_2$, $P[CH_2CH_2P(CH_3)_2]_3$, $[(CH_3)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(CH_3)_2]_2$, and their phosphine sulfide precursors are simple doublets in accord with equivalent $(CH_3)_2P$ methyls split by the single phosphorus atom. However, the $(CH_3)_2P$ proton resonances in $C_6H_5P[CH_2CH_2P(CH_3)_2]_2$, $(CH_3)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(CH_3)_2$, the previously reported[19] $C_6H_5P(CH_2CH_2PH_2)[CH_2CH_2P(CH_3)_2]$, and their phosphine sulfide precursors exhibit three or four lines. Comparison of the $(CH_3)_2P$ regions of the proton nmr spectra of these three polyphosphines at 60 and 100 MHz indicates that these complexities arise from slightly different chemical shifts of the two methyl groups in the $(CH_3)_2P$ unit rather than from coupling of the methyl protons in the $(CH_3)_2P$ unit to a second phosphorus atom. In $C_6H_5P[CH_2CH_2P(CH_3)_2]_2$, $(CH_3)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(CH_3)_2$, and $C_6H_5P(CH_2CH_2PH_2)[CH_2CH_2P(CH_3)_2]$, the $(CH_3)_2PCH_2CH_2$ unit is bonded to an asymmetric trivalent phosphorus atom bearing a phenyl ring and a saturated carbon bridge. This apparently makes the two diastereotopic[24] methyl groups in the $(CH_3)_2PCH_2CH_2$ unit sufficiently different for their nonequivalence to be detected by proton nmr spectroscopy. However, bonding a $(CH_3)_2PCH_2CH_2$ unit to an asymmetric trivalent phosphorus atom bearing a saturated carbon bridge and a second saturated carbon atom either from a methyl group (*e.g.* $CH_3P[CH_2CH_2P(CH_3)_2]_2$) or a second nonequivalent saturated carbon bridge (*e.g.* $[(CH_3)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(CH_3)_2]_2$) does not make the two diastereotopic methyl groups in such a $(CH_3)_2PCH_2CH_2$ unit sufficiently different for their nonequivalence to be detected by proton nmr spectroscopy.

The phosphorus-31 nmr resonances from $(C_6H_5)_2PCH_2CH_2$-, $C_6H_5P(CH_2CH_2-)_2$, and $P(CH_2CH_2-)_3$ units in methylated poly(tertiary phosphines) (Table II) occur at +13.1 to +13.2, +17.4 to +17.6, and +19.5 to +19.6 ppm, respectively, consistent with the previously observed[4] ranges in the phenylated poly(tertiary phosphines) except for some upfield shifts arising from the effects of such units being bonded to phosphorus atoms bearing some methyl groups rather than only phenyl groups as in the phenylated poly(tertiary phosphines). Units of the types $CH_3P(CH_2CH_2-)_2$ and $(CH_3)_2PCH_2CH_2$- exhibit characteristic phosphorus-31 resonances at +32.6 to +34.3 and at +46.5 to +48.8 ppm, respectively. In $(CH_3)_2PCH_2CH_2P<$ units the $^2J(PH)$ methyl-phosphorus coupling of ~2 Hz is so small relative to the $^3J(PP)$ phosphorus-phosphorus coupling of ~20 Hz, that even without proton decoupling the phosphorus resonances are clear doublets.

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Organometallic Chemistry of the Transition Metals. XXIX. Redox Systems in Hexamethylbenzene Cluster Compounds of Niobium and Tantalum[1-3]

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Abstract: Oxidation of the hexamethylbenzene niobium and tantalum clusters $[(Me_6C_6)_3M_3X_6]^+$ (M = Nb, X = Cl and Br; M = Ta, X = Cl) with reagents such as cerium(IV), *N*-bromosuccinimide, iodine, or air in acid solution or by electrochemical methods gives the corresponding diamagnetic clusters $[(Me_6C_6)_6M_6X_{12}]^{4+}$ isolable as their hexafluorophosphate or thiocyanate salts. The electrochemical reversibility of these redox systems is demonstrated by triangular voltammetry. All of the hexamethylbenzene niobium and tantalum clusters exhibit characteristic maxima in their electronic spectra which can be used for their identification in solution.

Since 1955 Fischer and coworkers have developed the "reducing Friedel-Crafts synthesis" for the preparation of bisarenemetal complexes of chromium,[6] molybdenum,[7] tungsten,[7] vanadium,[8] technetium,[9] rhenium,[10] iron,[11] ruthenium,[12] cobalt,[13] and rhodium[13] by reactions of the appropriate metal halides with an aromatic hydrocarbon in the presence of an anhydrous aluminum halide with aluminum powder as a reducing agent when necessary. However, when Fischer and Röhrscheid[14] attempted a similar method for the synthesis of hexamethylbenzene complexes of the early transition metals titanium, zirconium, niobium, and tantalum, they obtained products with only one rather than two arene units for each metal atom. All four of these metals thus gave apparent trimetallic cations of the stoichiometry $[(Me_6C_6)_3M_3Cl_6]^+$ (M = Ti, Zr, Nb, and Ta).

The niobium and tantalum compounds of Fischer and Röhrscheid[14] attracted our attention for several reasons. Their trimetallic formulas correspond to half of the well-known clusters containing M_6X_{12} units with an octahedron of six metal atoms bridged by halogen atoms across each of its 12 edges.[18] Indeed, at the time we began our work, the available data did not exclude unambiguously a hexametallic formulation for the niobium and tantalum hexamethylbenzene clusters although somewhat ambiguous molecular weight determinations made a trimetallic formulation more probable than a hexametallic one.[14] Furthermore, the or-