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Some 1:1 Base-Catalyzed Addition Reactions of Compounds Containing Two or More Phosphorus-Hydrogen Bonds to Various Vinylphosphorus Derivatives

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Abstract: Some 1:1 base-catalyzed additions of primary phosphines to vinylphosphorus compounds are discussed. Treatment of the primary phosphines RPH_2 (R = phenyl, *n*-hexyl, and neopentyl) with $CH_2{=}CHP(O)(OCHMe_2)_2$ in a 1:1 mole ratio in the presence of potassium *tert*-butoxide followed by $LiAlH_4$ reduction of the intermediate gives the corresponding secondary-primary diphosphines $RP(H)CH_2CH_2PH_2$. A similar reaction sequence with methylphosphine gives only the new tertiary-diprimary triphosphine $CH_3P(CH_2CH_2PH_2)_2$. Base-catalyzed 1:1 addition of $C_6H_5PH_2$ to $CH_2{=}CHP(S)(CH_3)_2$ gives crystalline $C_6H_5P(H)CH_2CH_2P(S)(CH_3)_2$ which undergoes desulfurization with $LiAlH_4$ in boiling dioxane to give $C_6H_5P(H)CH_2CH_2P(CH_3)_2$. Attempts to carry out a base-catalyzed 1:1 addition of $C_6H_5PH_2$ to $CH_2{=}CHP(C_6H_5)_2$ give mainly the known 1:2 adduct $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$, although a low yield of the corresponding 1:1 adduct $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ can be isolated under optimum conditions. A much more efficient conversion of $C_6H_5PH_2$ to $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ uses the base-catalyzed 1:1 addition of $C_6H_5PH_2$ to $CH_2{=}CHP(S)(C_6H_5)_2$ followed by $LiAlH_4$ desulfurization in boiling dioxane. Base-catalyzed 1:1 additions of $(C_6H_5)_2PCH_2CH_2PH_2$ and $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ to $CH_2{=}CHP(O)(OCHMe_2)_2$ give the tertiary-secondary-primary triphosphines $(C_6H_5)_2PCH_2CH_2P(H)CH_2CH_2PH_2$ and $C_6H_5P(H)CH_2CH_2P(C_6H_5)CH_2CH_2PH_2$, respectively, after $LiAlH_4$ reduction. Base-catalyzed addition of $(CH_3)_2PH$ to $CH_2{=}CHP(O)(OCHMe_2)_2$ followed by $LiAlH_4$ reduction gives the new tertiary-primary diphosphine $(CH_3)_2PCH_2CH_2PH_2$, which undergoes a base-catalyzed 1:1 addition to $CH_2{=}CHP(O)(OCHMe_2)_2$ to give the tertiary-secondary-primary triphosphine $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2$. A similar base-catalyzed 1:1 addition occurs at the secondary rather than a primary phosphorus atom in the secondary-primary diphosphine $C_6H_5P(H)CH_2CH_2PH_2$. For example, the base-catalyzed 1:1 addition of $C_6H_5P(H)CH_2CH_2PH_2$ to $CH_2{=}CHP(S)(CH_3)_2$ followed by desulfurization with $LiAlH_4$ in boiling dioxane gives $C_6H_5P(CH_2CH_2PH_2)[CH_2CH_2P(CH_3)_2]$. The infrared, proton and ^{31}P nmr, and mass spectra of new organophosphorus compounds arising from this work are discussed as well as some general aspects of the mechanism of their formation.

Previous papers from this laboratory have discussed the preparation of organophosphorus compounds containing PCH_2CH_2P units by the base-catalyzed additions of phosphorus-hydrogen bonds to vinylphosphines,[2,3] vinylphosphonates,[4-6] and vinylphosphine sulfides.[7] This paper describes a more detailed study of base-catalyzed additions of phosphorus-hydrogen compounds containing two or more phosphorus-hydrogen bonds to vinylphosphorus compounds. We sought methods where a single phosphorus-hydrogen bond in a compound containing two or more phosphorus-hydrogen bonds could be made to react selectively with a vinyl-phosphorus derivative under base-catalyzed conditions with retention of the remaining phosphorus-hydrogen bonds. Development of such methods significantly increases the range of organophosphorus compounds containing two or more phosphorus atoms that can be prepared by base-catalyzed additions of phosphorus-hydrogen bonds to vinylphosphorus compounds. The only related reactions reported in the literature[8] involve the treatment of primary phosphines RPH_2 with vinylphosphines $CH_2{=}CHPR'_2$ to give the tertiary-secondary diphosphines $RPHCH_2CH_2PR'_2$, but these reactions all occur under free-radical rather than base-catalyzed conditions and cannot be controlled to form the 1:1 adducts $RPHCH_2CH_2PR'_2$ without forming appreciable quantities of the 1:2 adducts $RP(CH_2CH_2PR'_2)_2$.

Experimental Section

Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga., and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were taken in capillaries and are uncorrected. For air-sensitive compounds, the melting point capillaries were loaded in a nitrogen-filled glove bag, and the open end was sealed with stopcock grease. Infrared spectra of the liquid compounds were taken between NaCl plates and recorded on a Perkin-Elmer Model 621 spectrometer. Proton and phosphorus-31 nmr spectra were taken as pure liquids or C_6D_6 solutions on a Varian HA-100 spectrometer at 100 and 40 MHz., respectively. Phosphorus chemical shifts are quoted as parts per million (ppm) upfield from external 85% H_3PO_4. Mass spectra were taken at 70 eV on a Perkin-Elmer Hitachi RMU-6 spectrometer. Relative intensities are given in parentheses after the ion formula.

A nitrogen atmosphere was always provided for the following operations: (a) carrying out reactions, (b) handling air-sensitive compounds, (c) filling evacuated vessels containing potentially air-sensitive materials. When necessary, a polyethylene glove bag containing pure nitrogen was used to provide this inert atmosphere. Other precautions are described elsewhere.[6]

The reagents RPH_2 (R = C_6H_5,[9] CH_3,[10] and $(CH_3)_3CCH_2$[11]), $CH_2{=}CHP(O)(OCHMe_2)_2$,[12] $CH_2{=}CHP(S)R_2$ (R = CH_3[7] or C_6H_5[13]), $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$,[14] $(C_6H_5)_2PCH_2CH_2PH_2$,[4,6] and $(CH_3)_2P(S)P(S)(CH_3)_2$[15] were prepared by published procedures. *n*-Hexylphosphine was prepared by the $LiAlH_4$ reduction of *n*-$C_6H_{13}P(O)(OCHMe_2)_2$,[16] which was obtained in 71% yield by the Arbusov reaction between *n*-hexyl bromide and triisopropyl phosphite. Tetrahydrofuran, dioxane, and diethyl ether were purified by distillation over sodium benzophenone ketyl under nitrogen.

Preparation of $C_6H_5P(H)CH_2CH_2PH_2$ from $C_6H_5PH_2$ and $CH_2{=}CHP(O)(OCHMe_2)_2$. A solution of 10.6 g (96.4 mmol) of phenylphosphine in 250 ml of tetrahydrofuran was treated with solid potassium *tert*-butoxide (about four spatula tips, ~0.2 g) until the mixture became yellow. The mixture was then heated to boiling under reflux and treated dropwise with a solution of 18.5 g (96.4 mmol) of diisopropyl vinylphosphonate in 75 ml of tetrahydrofuran over a period of 2 hr. During the addition of the first 15 ml of the diisopropyl vinylphosphonate solution, the yellow color of the reaction mixture was maintained by adding more potassium *tert*-butoxide when necessary. After all of the diisopropyl vinylphosphonate had been added, solvent was removed from the reaction mixture at ~25° (25 mm) and the residue dried at 25° (0.1 mm) for 4 hr to give 27 g (93% yield) of a glassy material with an nmr spectrum consistent with the 1:1 adduct $C_6H_5P(H)CH_2CH_2P(O)(OCHMe_2)_2$.

A solution of this residue in 100 ml of diethyl ether was added dropwise with stirring to 6.0 g (158 mmol) of $LiAlH_4$ in ~150 ml of diethyl ether. Vigorous bubbling occurred. The reaction mixture was stirred at room temperature for 2 hr. By then most of the bubbling had stopped. In order to assure complete reduction an additional 1.0 g (26.3 mmol) of $LiAlH_4$ was added and the mixture stirred for an additional 2 days at room temperature. The reaction mixture was then hydrolyzed by the successive additions of 7 ml of water, 7 ml of 15% aqueous sodium hydroxide, and 21 ml of water. The mixture was then filtered in a nitrogen atmosphere using a three-necked flask with a fritted disk and stopcock at the bottom.[6] Solvent was removed from the filtrate at ~25° (35 mm). Vacuum distillation of the residue gave 7.06 g (43% yield) of $C_6H_5P(H)CH_2CH_2PH_2$, bp 79-80° (0.35 mm). This product was identified by comparison of its proton and ^{31}P nmr spectra with those reported[6] for authentic $C_6H_5P(H)CH_2CH_2PH_2$.

Preparation of *n*-$C_6H_{13}P(H)CH_2CH_2PH_2$ from *n*-$C_6H_{13}PH_2$ and $CH_2{=}CHP(O)(OCHMe_2)_2$. Reaction of 15.5 g (131 mmol) of *n*-hexylphosphine with 25.2 g (131 mmol) of $CH_2{=}CHP(O)(OCHMe_2)_2$ in the presence of catalytic potassium *tert*-butoxide (six spatula tips, ~0.3 g, no yellow color observed in this case) followed by reduction of the white cloudy liquid intermediate with 8.0 g (210 mmol) of $LiAlH_4$ in a total of 350 ml of diethyl ether using the general procedure given above for the preparation of $C_6H_5P(H)CH_2CH_2PH_2$ from $C_6H_5PH_2$ and $CH_2{=}CHP(O)(OCHMe_2)_2$ gave 7.2 g (31% yield) of colorless foul-smelling liquid *n*-$C_6H_{13}P(H)CH_2CH_2PH_2$, bp 121-123° (12 mm).

Anal. Calcd for $C_8H_{20}P_2$: C, 54.0; H, 11.2; P, 34.8. Found: C, 53.9; H, 11.1; P, 34.7.

Infrared spectrum: ν(CH) frequencies at 2960 (m), 2930 (s), 2873 (m), and 2858 (m); ν(PH) frequency at 2293 (m); other bands at 1465 (w), 1456 (w), 1421 (w), 1378 (vw), 1261 (vvw), 1180 (vw), 1112 (vw), 1080 (w), 843 (vw), and 811 (vw) cm^{-1}. Proton nmr spectrum: resonances at τ 6.93 (doublet of broad peaks, J_D = 195 Hz), 7.27 (doublet of triplets with obscured higher peak, J_D = 185, J_T = 7 Hz), 8.3 (complex), 8.45-8.75 (broad, complex), and 9.14 (triplet, J = 6 Hz) of approximate relative intensities 1:2:4:10:3 assigned to the PH, PH_2, PCH_2CH_2P, *n*-hexyl CH_2, and *n*-hexyl CH_3 protons, respectively. Phosphorus-31 nmr spectrum: resonances at +66.1 (doublet, J = 1.95 Hz) and +130.1 ppm (triplet, J = 185 Hz) assigned to the PH and PH_2 phosphorus atoms, respectively. Mass spectrum (chamber temperature 210°, sample temperature 110°): $C_6H_{13}PHCH_2CH_2PH_2^+$ (100), $C_6H_{13}P_2H_3^+$ (56), $C_6H_{13}P_2H_2^+$ (21), $C_6H_{13}PHCH_2CH_2^+$ (100), $C_4H_9P_2H_2^+$ (22), $C_6H_{13}PH_2^+$ (29), $C_6H_{13}PH^+$ (107), $C_6H_{13}P^+$ (49), $H_2PCH_2CH_2PH_2^+$ (100), $HPCH_2CH_2PH_2^+$ (71), $C_6H_8^+$ and/or $CH_2P_2H_4^+$ (120), $C_5H_6^+$ and/or $P_2H_4^+$ (140), $C_5H_5^+$ and/or $P_2H_3^+$ (68), $C_2H_5PH_2^+$ (86), $C_2H_4PH_2^+$ (135), $C_2H_4P^+$ (100), $C_4H_9^+$ and/or $C_2H_2P^+$ (93), $C_4H_7^+$ (93), $CH_3PH_2^+$ (230), $C_3H_7^+$ (170), $C_3H_5^+$·(200), and $C_3H_3^+$ (71); metastable ions at *m/e* 126.3 m ($C_6H_{13}PHCH_2CH_2PH_2^+ \rightarrow C_6H_{13}P_2H_3^+ + C_2H_4$), 89.8 m ($C_6H_{13}P_2H_3^+ \rightarrow C_6H_{13}P^+ + PH_3$), 49.6 w ($C_6H_{13}PHCH_2CH_2PH_2^+ \rightarrow H_2PCH_2CH_2PH_2^+ + C_6H_{12}$), 46.2 w ($H_2PCH_2CH_2PH_2^+ \rightarrow P_2H_4^+ + C_2H_4$), and 37.2 w ($HPCH_2CH_2PH_2^+ \rightarrow C_2H_4P^+ + PH_3$).

Preparation of $(CH_3)_3CCH_2P(H)CH_2CH_2PH_2$ from $(CH_3)_3CCH_2PH_2$ and $CH_2{=}CHP(O)(OCHMe_2)_2$. Reaction of 5.59 g (53.6 mmol) of neopentylphosphine with 10.3 g (53.6 mmol) of $CH_2{=}CHP(O)(OCHMe_2)_2$ in the presence of catalytic potassium *tert*-butoxide (no yellow color observed in this case) followed by reduction of the intermediate with 4.0 g (105 mmol) of $LiAlH_4$ in a total of 200 ml of diethyl ether using the general procedure given above for the preparation of $C_6H_5P(H)CH_2CH_2PH_2$ from $C_6H_5PH_2$ and $CH_2{=}CHP(O)(OCHMe_2)_2$ gave 2.87 g (33% yield) of liquid $(CH_3)_3CCH_2P(H)CH_2CH_2PH_2$, bp 63° (3.5 mm), with a superimposed sweet and foul odor.

Anal. Calcd for $C_7H_{18}P_2$: C, 51.1; H, 11.0; P, 37.8. Found: C, 51.4; H, 10.8; P, 37.8.

Infrared spectrum: ν(CH) frequencies at 2959 (s), 2910 (m), 2896 (m), and 2870 (m); ν(PH) frequency at 2290 (s); other bands at 1475 (m), 1466 (m), 1421 (w), 1390 (w), 1366 (m), 1263 (vw), 1245 (w), 1179 (w), 1128 (w), 1103 (vw, sh), 1080 (m), 1030 (w), 936 (vw), 917 (vw), ~850 (br, vw, sh), and 822 (vw) cm^{-1}; Proton nmr spectrum: PH resonances at τ 7.03 (doublet of multiplets with the upper half obscured, $J_D \approx$ 186 Hz), PH_2 resonance at τ 7.31 (doublet of multiplets with the upper half obscured, $J_D \approx$ 188 Hz), CH_2 resonance at τ 8.3 (broad), and CH_3 resonance at τ 9.01 (sharp singlet). Phosphorus-31 nmr spectrum: resonances at +79.1 (doublet, J_D = 186 ± 6 Hz) and +130.4 ppm (doublet of multiplets, J_D = 188 ± 6 Hz, $J_M \approx$7 Hz) corresponding to the PH and PH_2 phosphorus atoms, respectively. Mass spectrum (chamber temperature 100°, sample temperature 95°): $(CH_3)_3CCH_2PHCH_2CH_2PH_2^+$ (87), $(CH_3)_3CCH_2P_2H_3^+$ (100), $(CH_3)_3CCH_2P_2H_2^+$ (40), $(CH_3)_3CCH_2PHCH_2CH_2^+$ (44), $(CH_3)_3CCH_2P^+$ (40), $HPCH_2CH_2PH_2^+$ (115), $CH_2P_2H_4^+$ (84), $CH_2P_2H_3^+$ (24), $C_3H_7PH^+$ (29), $(CH_3)_3CCH_2^+$ (67), $C_5H_5^+$ and/or $P_2H_3^+$ (40), $C_2H_5PH_2^+$ (56), $C_2H_4PH_2^+$ (42), $C_2H_4P^+$ (33), $C_4H_9^+$ and/or $C_2H_2P^+$ (120), CH_2P^+ (29), $C_3H_7^+$ (95), C_3H_5 (98), and $C_3H_3^+$ (31); metastable ions at *m/e* 112.9 s ($(CH_3)_3CCH_2PHCH_2CH_2PH_2^+ \rightarrow (CH_3)_3CCH_2P_2H_3^+ + C_2H_4$), 111.0 s ($(CH_3)_3CCH_2PHCH_2CH_2PH_2^+ \rightarrow (CH_3)_3CCH_2P_2H_2^+ + C_2H_5$), 76.6 m ($(CH_3)_3CCH_2P_2H_3^+ \rightarrow (CH_3)_3CCH_2P^+ + PH_3$), and 37.3 w ($HPCH_2CH_2PH_2^+ \rightarrow C_2H_4P^+ + PH_3$).

Reaction of CH_3PH_2 with $CH_2{=}CHP(O)(OCHMe_2)_2$. Methylphosphine was generated by the dropwise additon of a solution of 32.3 ml (37.2 g, 300 mmol) of dimethyl methylphosphonate in 50 ml of dioxane to a mixture of 12 g (316 mmol) of $LiAlH_4$ and 250 ml of dioxane.[10] This methylphosphine was trapped in a flask cooled to −78° containing 200 ml of tetrahydrofuran with 0.3 g of added potassium *tert*-butoxide. After all of the methylphosphine had been collected, the reaction mixture was heated to boiling under a −78° reflux condenser. A solution of 24.0 g (125 mmol) of diisopropyl vinylphosphonate in 50 ml of tetrahydrofuran was added dropwise to the refluxing reaction mixture. During this process the rate of reflux of the methylphosphine markedly decreased indicating its consumption. The reaction mixture was boiled under reflux for an additional 2 hr after completion of the diisopropyl vinylphosphonate addition. Excess methylphosphine was removed in a nitrogen stream and excess tetrahydrofuran at 25° (0.1 mm) (*caution:* solvent trapped at −78° because of remaining methylphosphine and other malodorous materials). The residue in 100 ml of diethyl ether was added dropwise to 8.0 g (210 mmol) of $LiAlH_4$ in 200 ml of diethyl ether. After stirring at room temperature for 2 days, the mixture was hydrolyzed by the successive addition of 8 ml of water, 8 ml of 15% aqueous sodium hydroxide, and 24 ml of water. Filtration under nitrogen, removal of the diethyl ether at 25° (35 mm), and vacuum distillation gave first a forerun of 1.5 g of a pyrophoric liquid, bp 35-40° (10 mm) and then 1.2 g (11% yield) of liquid $CH_3P(CH_2CH_2PH_2)_2$, bp 70° (0.6 mm).

Anal. Calcd for $C_5H_{15}P_3$: C, 35.7; H, 8.9. Found: C, 36.5; H, 8.9.

Infrared spectrum: ν(CH) frequencies at 2953 (w), 2931 (w), 2909 (m), 2900 (m), 2880 (w), and 2811 (vw) cm; ν(PH) frequency at 2289 (m); other bands at 1419 (m), 1283 (w), 1173 (w), 1110 (w), 1075 (m), 945(vw), 870 (w), 846 (w), 776 (w), 738 (vw), 697 (w), and 668 (w) cm^-. Proton nmr spectrum: PH_2 resonance at τ 7.24 (doublet of multiplets, $J_D = 192$ Hz), CH_2 resonance at 8.42 (multiplet, seven discernible lines), and CH_3 resonance at 9.05 (doublet, $J = 3$ Hz). Phosphorus-31 nmr spectrum: resonances at +31.5 (singlet) and +126.2 ppm (triplet of apparent septets; $J_T = 190 \pm 3$, $J_{sep} = 7$ Hz) corresponding to the single tertiary phosphorus atom and the two primary phosphorus atoms, respectively. Mass spectrum (chamber temperature 210°, sample temperature 110°): $CH_3P(CH_2CH_2PH_2)_2^+$ (6), $CH_3P(CH_2CH_2PH_2)(CH_2CH_2PH)^+$ (4), $CH_3P(CH_2CH_2PH_2)CH_2CH_2^+$ (100), $CH_3PCH_2CH_2PH_2^+$ (24), $CH_3P(C_2H_3)CH_2CH_2^+$ (6), $H_2PCH_2CH_2PH_2^+$ (8), $HPCH_2CH_2PH_2^+$ (6), $H_2P(CH_2CH_2)_2^+$ (9), $CH_3P_2H_3^+$ (34), $CH_3P_2H_2^+$ (32), $CH_3P_2H^+$ (7), $C_3H_{10}P^+$ (15), $C_3H_9P^+$ (10), $C_3H_8P^+$ (19), $C_3H_7P^+$ (8), $C_3H_6P^+$ (19), $C_2H_8P^+$ (7), $C_2H_7P^+$ (16), $C_2H_6P^+$ (21), $C_2H_4P^+$ (20), $C_2H_2P^+$ (25), and CH_2P^+ (45); metastable ions at *m/e* 108.7 s ($CH_3P(CH_2CH_2PH_2)_2^+ \rightarrow CH_3P(CH_2CH_2PH_2)CH_2CH_2^+ + PH_2$), 75.6 m ($CH_3P(CH_2CH_2PH_2)CH_2CH_2^+ \rightarrow CH_3P(C_2H_3)CH_2CH_2^+ + PH_3$), 58.3 m ($CH_3PCH_2CH_2PH_2^+ \rightarrow CH_3P_2H_2^+ + C_2H_4$), 52.8 w ($CH_3P(C_2H_3)CH_2CH_2^+ \rightarrow CH_3PC_2H_3^+ + C_2H_4$), 41.7 w ($H_2P(CH_2CH_2)_2^+ \rightarrow C_2H_4PH_2^+ + C_2H_4$). and 39.5 vw ($H_2PCH_2CH_2PH_2^+ \rightarrow C_2H_4PH_2^+ + PH_2$).

If the reaction of methylphosphine with diisopropyl vinylphosphonate was carried out at 40° rather than at the boiling point of the tetrahydrofuran using otherwise identical reaction conditions, only unchanged diisopropyl vinylphosphonate was recovered.

Preparation of $C_6H_5P(H)CH_2CH_2P(S)(CH_3)_2$. A solution of 11.0 g (100 mmol) of phenylphosphine in 200 ml of tetrahydrofuran was treated with sufficient potassium *tert*-butoxide (~0.3 g) to give a persistent bright yellow to orange color. The solution was then heated to the boiling point under reflux and treated dropwise with a solution of 12.0 g (100 mmol) of dimethylvinylphosphine sulfide in 50 ml of tetrahydrofuran. During the addition of the dimethylvinylphosphine sulfide, additional potassium *tert*-butoxide catalyst (2 × 0.3 g) was added to maintain a yellow color. After the addition of the dimethylvinylphosphine sulfide was complete, the reaction mixture was boiled under reflux for an additional 30 min. Tetrahydrofuran was then removed at 25° (0.1 mm) (the solvent was trapped since it had a phenylphosphine odor). The solid residue was dissolved in hot degassed ethanol. The filtered solution was allowed to stand at room temperature. The crystals which separated were filtered under nitrogen and dried at 25° (0.1 mm) for 24 hr to give a total of 19.5 g (85% yield) of white crystalline $C_6H_5P(H)CH_2CH_2P(S)(CH_3)_2$, mp 92-93°, collected in two crops.

Anal. Calcd for $C_{10}H_{16}P_2S$: C, 52.2; H, 7.0; S, 13.9. Found: C, 52.1; H, 7.1; S, 14.1.

Proton nmr spectrum: phenyl resonances at τ 2.71 (multiplet) and 2.94 (multiplet) of 2:3 relative intensities, PH resonance at τ 6.01 (doublet of broad resonances, $J = 202$ Hz), CH_2 resonances at τ 8.13 (broad) and 8.45 (complex multiplet) of 1:1 relative intensities, and CH_3 resonance at τ 8.90 (doublet, $J = 14$ Hz).

Desulfurization of $C_6H_5P(H)CH_2CH_2P(S)(CH_3)_2$ to $C_6H_5P(H)CH_2CH_2P(CH_3)_2$. A mixture of 17.5 g (76 mmol) of $C_6H_5P(H)CH_2CH_2P(S)(CH_3)_2$, 2.0 g (53 mmol) of $LiAlH_4$, and 150 ml of dioxane was boiled under reflux with stirring for 21 hr adding 1.0 g (26 mmol) more of $LiAlH_4$ after 3 hr of boiling. The reaction mixture, after cooling, was hydrolyzed by successive additions of 3 ml of water, 3 ml of 15% aqueous sodium hydroxide, and 9 ml of water. The hydrolyzed mixture was allowed to stand for 2 days and then filtered under nitrogen in a closed three-necked flask with a stopcock and fritted disk at the bottom. The filtrate was then distilled after removal of the dioxane and diethyl ether (used to wash the precipitate) to give 8.13 g (57% yield) of $C_6H_5P(H)CH_2CH_2P(CH_3)_2$, bp 86° (0.2 mm).

Anal. Calcd for $C_{10}H_{16}P_2$: C, 60.6; H, 8.1; P, 31.3. Found: C, 60.4; H, 8.1; P, 31.2.

Infrared spectrum: ν(CH) frequencies at 3172 (w), 3156 (w), 3015 (vw), 3007 (vw), 2955 (m), 2936 (vw), 2897 (m), and 2814 (w); ν(PH) frequency at 2285 (m); other bands at 1483 (w), 1433 (m), 1422 (m), 1293 (w), 1276 (w), 1172 (w), 1108 (w), 1095 (w), 1070 (vw), 1026 (w), 1000 (vw), 938 (m), 893 (w), 873 (w), 845 (w), 815 (vw), and 738 (m) cm^{-1}. Proton nmr spectrum: phenyl resonances at τ 2.68 (multiplet) and 2.90 (multiplet) of approximate relative intensities 2:3, PH resonance at τ 5.90 (doublet of multiplets, $J_D \approx 204$ Hz.), CH_2 resonances at τ 8.24 (multiplet) and 8.63 (multiplet) of approximate relative intensities 1:1, and methyl resonance at τ 9.18 (doublet, $J = 4$ Hz.). A double resonance experiment with irradiation at the frequency of the $(CH_3)_2P$ phosphorus atom converted the τ 5.90 PH resonance into a doublet of triplets ($J_T = 7$ Hz) and the τ 9.18 $(CH_3)_2P$ resonance into a sharp singlet. Phosphorus-31 nmr spectrum: resonances at +43.6 (broad singlet) and +46.5 ppm (doublet, $J \approx 204$ Hz) from the tertiary and secondary phosphorus atoms, respectively.

Mass spectrum (chamber temperature 100°, sample temperature 100°): $C_6H_5P(H)CH_2CH_2P(CH_3)_2^+$ (79), $C_6H_5P(H)CH_2CH_2PCH_3^+$ (6), $C_6H_5P(H)P(CH_3)_2^+$ (53), $C_{10}H_{14}P^+$ (100), $C_6H_5P(H)PCH_3^+$ (15), $C_9H_{13}P^+$ (32), $C_9H_{10}P^+$ (6), $C_8H_{11}P^+$ (45), $C_6H_5P(H)CH_2CH_2^+$ (36), $C_7H_9P^+$ (28), $(CH_3)_2PCH_2CH_2PH^+$ (17), $C_6H_6P^+$ (79), $C_6H_5P^+$ (40), $C_6H_4P^+$ (47), $C_7H_7^+$ (45), $C_7H_5^+$ (53), $C_4H_4P^+$ (30), $C_6H_5^+$ (25), $C_6H_4^+$ (60), $C_5H_5^+$ (30), $C_2H_6P^+$ (64), $C_2H_4P^+$ (43), $C_2H_2P^+$ (45), $C_4H_3^+$ (21), CH_2P^+ (47), $C_3H_5^+$ (28), and $C_3H_3^+$ (28). Metastable ions at *m/e* 146 s ($C_6H_5P(H)CH_2CH_2P(CH_3)_2^+ \rightarrow C_6H_5P(H)P(CH_3)_2^+ + C_2H_4$), 131.5 w ($C_6H_5P(H)CH_2CH_2PCH_3^+ \rightarrow C_6H_5P(H)PCH_3^+ + C_2H_4$), 110.3 m ($C_6H_5P(H)P(CH_3)_2^+ \rightarrow C_6H_5PC_2H_5^+ + PH_2$), 109.5 w ($C_6H_5P(CH_3)_2^+ \rightarrow C_6H_5PCH_3^+ + CH_3$), 86.7 w ($C_6H_5PC_2H_5^+ \rightarrow C_6H_6P^+ + C_2H_4$), and 54.4 w ($C_6H_6P^+ \rightarrow C_6H_5^+ + PH$).

Isolation of $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ from the Reaction of $C_6H_5PH_2$ with $CH_2{=}CHP(C_6H_5)_2$. A boiling solution of 5.17 g (47 mmol) of phenylphosphine in 200 ml of tetrahydrofuran containing sufficient potassium *tert*-butoxide (two to three spatula tips, ~0.15 g) to give a deep yellow color was treated dropwise with a solution of 10.0 g (47 mmol) of diphenylvinylphosphine in 50 ml of tetrahydrofuran over 1.5 hr. After boiling under reflux for an additional 16 hr, the solvent was removed from the reaction mixture at 0.1 mm. The residue was treated with ~200 ml of degassed pentane. The solid which formed was filtered at 0° and dried to give 3.5 g of the tritertiary phosphine $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$, mp 129-130° (lit.[3] mp 125-126°). The pentane filtrate was evaporated at ~25° (35 mm) and the residue was treated with 75 ml of degassed ethanol. The solid which formed was filtered and dried to give an additional 5.7 g of the tri(tertiary phosphine) $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$, mp 126-127°. Evaporation of the ethanol filtrate at 25° (35 mm) gave 2.0 g of a liquid indicated by its proton nmr spectrum to be nearly pure $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$. The yields of $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ and $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ from this reaction thus were 72 and 13%, respectively.

Preparation of $C_6H_5P(H)CH_2CH_2P(S)(C_6H_5)_2$ from $C_6H_5PH_2$ and $CH_2{=}CHP(S)(C_6H_5)_2$. A solution of 3.2 g (29 mmol) of phenylphosphine in 50 ml of tetrahydrofuran was treated with sufficient potassium *tert*-butoxide (two spatula tips, ~0.1 g) to give a deep yellow color. This solution was heated to boiling under reflux, and then treated dropwise with a solution of 7.1 g (29 mmol) of diphenylvinylphosphine sulfide in 37 ml of tetrahydrofuran over a period of 1.5 hr. Additional potassium *tert*-butoxide was added to restore the yellow color. The reaction mixture was boiled under reflux for an additional 15 hr. Solvent was then removed at 0.1 mm and trapped because of the odor of phenylphosphine. The thick pasty residue was dissolved in 100 ml of hot ethanol. Cooling the ethanol solution back to room temperature precipitated an oil. The ethanol was removed by decantation and the oil dried at 50° (0.1 mm) for 20 hr to give an essentially quantitative yield of $C_6H_5P(H)CH_2CH_2P(S)(C_6H_5)_2$.

Anal. Calcd for $C_{20}H_{20}P_2S$: C, 67.8; H, 5.6; S, 9.0. Found: C, 67.5; H, 5.7; S, 9.2.

Infrared spectrum: ν(CH) bands at 3148 (vw), 3059 (s), 3028 (sh), 2953 (vw), and 2914 (m); ν(PH) band at 2288 (s); other bands at 1963 (w), 1893 (w), 1816 (w), 1590 (m), 1577 (m), 1483 (s), 1431 (s), 1404 (sh), 1326 (sh), 1308 (s), 1266 (m), 1173 (s), 1097 (s), 1069 (m), 1025 (m), 997 (m), 945 (w), 926 (sh), 849 (w), 793 (w), 745-685 (vw, br), 616 (s), and 605 (s) cm^{-1}. Proton nmr spectrum: phenyl resonances at τ 2.41 (multiplet) and 2.98 (multiplet) of approximate relative intensities 4:11, respectively, PH resonance at τ 6.04 (doublet of triplets, $J_D = 206$, $J_T = 7$ Hz), and CH_2 resonances at τ 7.75 (broad) and 8.05 (broad) of approximate relative intensities 1:1.

Desulfurization of $C_6H_5P(H)CH_2CH_2P(S)(C_6H_5)_2$ to $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$. A mixture of 10.3 g (29 mmol) of $C_6H_5P(H)CH_2CH_2P(S)(C_6H_5)_2$, 2.0 g (53 mmol) of $LiAlH_4$, and 100 ml of dioxane was boiled under reflux for 24 hr with stirring. The reaction mixture was hydrolyzed by the successive addition of 2 ml of water, 2 ml of 15% aqueous sodium hydroxide, and 6 ml of water. The dioxane solution was then filtered and solvent removed at 0.1 mm. Vacuum distillation of the residue gave 5.4 g (57% yield) of $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$, bp 205-210° (0.1-0.2 mm) identified by comparison of its proton nmr spectrum with that of an authentic sample.[6]

Reaction of $(C_6H_5)_2PCH_2CH_2PH_2$ with $CH_2{=}CHP(O)(OCHMe_2)_2$ Followed by $LiAlH_4$ Reduction. A solution of 8.10 g (33 mmol) of $(C_6H_5)_2PCH_2CH_2PH_2$ in 150 ml of tetrahydrofuran containing sufficient potassium *tert*-butoxide to impart a yellow-orange color (~0.2 g) was treated dropwise at the boiling point with a solution of 6.32 g (33 mmol) of diisopropyl vinylphosphonate in 50 ml of tetrahydrofuran over 1.5 hr. After an additional 16.5 hr of boiling under reflux, solvent was removed at 40° (40 mm). The liquid residue was reduced with 2.0 g (53 mmol) of $LiAlH_4$ in 200 ml of diethyl ether at room temperature for 20 hr. Hydrolysis, solvent removal, and vacuum distillation (see the preparation of $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ immediately above) gave 3.15 g of a liquid, bp 175° (0.4 mm), shown by its proton and ^{31}P nmr spectra to be mainly unreacted $(C_6H_5)_2PCH_2CH_2PH_2$ and 1.88 g of a liquid, bp 180-185° (0.4 mm), exhibiting in its ^{31}P nmr spectrum a singlet at +14.2, a doublet (J = 193 Hz) at +61.1, a triplet (J = 187 Hz) at +127.8, and a triplet (J = 193 Hz) at +129.1 ppm and exhibiting in its proton nmr spectrum phenyl resonances at τ 2.85 and 3.0, the lower half of a PH doublet at τ 5.4 (very broad), two overlapping slightly nonequivalent PH_2 double triplets centered at $\tau \sim 7.4$ (J_T = 7 Hz), and two broad methylene resonances of equal relative intensities at τ 8.0 and 8.5. These nmr spectra including integration of the proton nmr spectrum suggested that this higher boiling fraction was a mixture of the $(C_6H_5)_2PCH_2CH_2PH_2$ starting material and the expected tertiary-secondary-primary triphosphine product $(C_6H_5)_2PCH_2CH_2P(H)CH_2CH_2PH_2$, which could not be separated by simple distillation.

Preparation of $(CH_3)_2PCH_2CH_2PH_2$. Dimethylphosphine[17] was generated by reaction of 55.8 g (300 mmol) of tetramethylbiphosphine disulfide with 18 g (474 mmol) of $LiAlH_4$ in 500 ml of dioxane in a 1-l. three-necked flask using external ice-water cooling to moderate the exothermic reaction. After the reduction was complete, the dimethylphosphine was distilled through a Vigreux column into a second 1-l. three-necked flask cooled to −78° and containing about 0.2 g of potassium *tert*-butoxide and 450 ml of redistilled tetrahydrofuran. This second flask was equipped with a −78° reflux condenser to prevent escape of the dimethylphosphine. In order to assure complete transfer of the dimethylphosphine into the reaction flask, the flask generating the dimethylphosphine was heated enough to reflux the dioxane solvent part way up the Vigreux column after the initial exothermic reaction had subsided.

After disconnecting the dimethylphosphine generator, the mixture of dimethylphosphine, tetrahydrofuran, and the potassium *tert*-butoxide catalyst was heated to 40-50° and treated with 86 g (448 mmol) of diisopropyl vinylphosphonate in 50 ml of tetrahydrofuran at such a rate to reflux gently the dimethylphosphine. About 30 min were required for this addition. The reaction mixture was then boiled under reflux for 14 hr with replacement of the −78° reflux condenser with a normal water-cooled reflux condenser after 1 hr of the refluxing. After cooling to room temperature at the end of the reflux period, solvent was removed at 25° (0.1 mm) collecting it in a −78° trap in order to prevent escape of excess dimethylphosphine. An orange liquid remained. The proton nmr spectrum of this liquid after redistillation at 83° (0.2 mm) exhibited a multiplet at τ 5.39, a doublet (J = 6 Hz) at 8.77, and a doublet (J = 2.7 Hz) at 9.05 assignable to the isopropyl methine, isopropyl methyl, and $(CH_3)_2P$ protons, respectively, of the expected adduct $(CH_3)_2PCH_2CH_2P(O)[OCH(CH_3)_2]_2$ as well as another doublet (J = 3.6 Hz) at τ 8.47 due to the methylphosphorus protons of an unidentified impurity and an underlying broad resonance at τ 8.5 assignable to the PCH_2CH_2P protons.

About 90% of the crude unredistilled adduct from the above reaction was dissolved in ~ 250 ml of diethyl ether and this solution added dropwise to 26 g (685 mmol) of $LiAlH_4$ in 400 ml of diethyl ether at 0°. The reaction mixture was stirred at room temperature for 14 hr and then hydrolyzed at 0° by the successive dropwise addition of 26 ml of water, 26 ml of 15% aqueous sodium hydroxide, and 78 ml of water. After filtration under nitrogen and removal of the diethyl ether at 30° (130-80 mm), distillation of the residue gave 22.8 g (48% yield) of colorless air-sensitive $(CH_3)_2PCH_2CH_2PH_2$, bp 55° (20 mm).

Anal. Calcd for $C_4H_{12}P_2$: C, 39.3; H, 9.8; P, 50.8. Found: C, 39.2; H, 9.9; P, 50.5.

Infrared spectrum: ν(CH) frequencies at 2965 (w), 2958 (m), 2898 (m), and 2815 (w); ν(PH) frequency at 2292 (s); other bands at 1425 (m), 1419 (m), 1291 (w), 1274 (w), 1196 (vw), 1174 (w), 1112 (w), 1094 (w), 1074 (m), 1018 (vw), 934 (m), 885 (w), 865 (w), 856 (w), 842 (w), 813 (w), 760 (w), 708 (m), 702 (m), and 670 (w) cm^{-1}. Proton nmr spectrum: PH_2 resonance at τ 7.26 (doublet of multiplets; J_D = 189 Hz); CH_2 resonance at τ 8.47 (complex multiplet), and CH_3 resonance at τ 9.07 (doublet, J = 2.9 Hz) of approximate relative intensities 2:4:6, respectively. Phosphorus-31 nmr spectrum: resonances at +49.7 (multiplet, ten discernible lines, $J_{\text{mult}} \approx 3$ Hz) and +127.8 ppm (triplet of septets, $J_T = 185 \pm 5$, $J_{\text{sep}} \approx 6$ Hz) from the tertiary and primary phosphorus atoms, respectively. Mass spectrum (chamber temperature 210°; sample temperature 60°): $(CH_3)_2PCH_2CH_2PH_2^+$ (33), $(CH_3)_2PCH_2CH_2PH^+$ (6), $CH_3PCH_2CH_2PH_2^+$ (1), $C_3H_7P_2^+$ (1), $(CH_3)_2P_2H_2^+$ (60), $(CH_3)_2P_2H^+$ (15), $(CH_3)_2PCH_2CH_2^+$ (56), $CH_3P_2H_2^+$ (14), $CH_3P_2^+$ (10), $C_3H_9P^+$ and/or $CH_2P_2^+$ (49), $C_3H_8P^+$ (15), $C_3H_6P^+$ (8), $C_2H_8P^+$ (10), $C_2H_7P^+$ (47), $C_2H_6P^+$ (100), $C_2H_4P^+$ (42), $C_2H_2P^+$ (43), CH_3PH^+ (13), CH_3P^+ (20), CH_2P^+ (47), $C_3H_5^+$ (8), and $C_2H_3^+$ (19). Metastable ions at m/e 72.5 s ($(CH_3)_2PCH_2CH_2PH_2^+ \rightarrow (CH_3)_2P_2H_2^+ + C_2H_4$), 41.8 vw ($(CH_3)_2PCH_2CH_2^+ \rightarrow (CH_3)_2P^+ + C_2H_4$), and 39.5 m ($(CH_3)_2P_2H_2^+ \rightarrow (CH_3)_2P^+ + PH_2$).

Preparation of $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2$ from $(CH_3)_2PCH_2CH_2PH_2$ and $CH_2 = CHP(O)(OCHMe_2)_2$. A solution of 10.33 g (85 mmol) of $(CH_3)_2PCH_2CH_2PH_2$, ~ 0.2 g of potassium *tert*-butoxide, and 200 ml of tetrahydrofuran was treated dropwise with a solution of 16.3 g (85 mmol) of $CH_2{=}CHP(O)(OCHMe_2)_2$ in 75 ml of tetrahydrofuran over a period of 1 hr while boiling under reflux. The reaction mixture was boiled under reflux for an additional 14 hr. Tetrahydrofuran was then removed at 30° (20 mm). The proton nmr spectrum of the resulting liquid exhibited resonances at τ 5.39 (multiplet), 6.83 (doublet of broad peaks, J_D = 191 Hz), 8.2-8.5 (broad, complex), 8.76 (doublet, J = 6 Hz), and 9.05 (doublet, J = 3 Hz), of approximate relative intensities 2:1:8:12:6, respectively, corresponding to the CH, PH, CH_2, isopropyl methyl, and CH_3P protons, respectively, of the expected adduct $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2P(O)(OCHMe_2)_2$.

A solution of the crude adduct in 100 ml of diethyl ether was added dropwise to 5 g (131 mmol) of $LiAlH_4$ in 100 ml of diethyl ether. After stirring for 14 hr at 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. After filtration under nitrogen and removal of the diethyl ether at 30° (20 mm), distillation of the residue gave 10.5 g (72% yield) of colorless liquid $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2$, bp 78-80° (0.2 mm).

Anal. Calcd for $C_6H_{17}P_3$: C, 39.5; H, 9.3; P, 51.1. Found: C, 39.2; H, 9.1; P, 50.7.

Infrared spectrum: ν(CH) frequencies at 2967 (m), 2957 (m), 2932 (m), 2897 (s), and 2816 (w); ν(PH) frequency at 2290 (s); other bands at 1427 (m), 1420 (m), 1291 (w), 1277 (w), 1265 (vw), 1178 (w), 1171 (w), 1107 (w), 1078 (m), 1020 (vw), 938 (m), 892 (w), 860 (w), 840 (w), 816 (w), and 701 (m) cm^{-1}. Proton nmr spectrum: PH resonance at τ 6.82 (doublet of triplets, J_D

= 192, J_T = 7 Hz), lower half of PH_2 resonance at τ 6.30 (triplet, J = 7 Hz), overlapping upper half of PH_2 resonance and CH_2 resonance at τ 8.2–8.6 (broad), and methyl resonance at τ 9.04 (doublet, J = 3 Hz) of approximate relative intensities 1:1:9:6, respectively. Phosphorus-31 nmr spectrum: resonances at +48.6 (doublet, $J \approx 17$ Hz), +60.1 (doublet, J = 192 Hz), and +128.9 ppm (triplet of multiplets, J_T = 193 Hz) corresponding to the tertiary, secondary, and primary phosphorus atoms, respectively. Mass spectrum (chamber temperature 210°, sample temperature 210°): $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2^+$ (2.8), $CH_3PCH_2CH_2P(H)CH_2CH_2PH_2^+$ (1.1), $(CH_3)_2P_3H_3C_2H_4^+$ (6.2), $(CH_3)_2P_3H_2C_2H_4^+$ (3.0), $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2^+$ (23), $C_3H_{10}P_3^+$ (0.9), $C_3H_8P_3^+$ (1.3), $C_3H_6P_3^+$ (2.8), $(CH_3)_2P_3H_3^+$ (5.7), $(CH_3)_2PCH_2CH_2PH^+$ (100), $(CH_3)_2P_2H^+$ (43), $(CH_3)_2PCH_2CH_2^+$ (28), $CH_3P_2^+$ (7.0), $C_3H_9P^+$ and/or $CH_2P_2^+$ (11), $C_3H_8P^+$ (7.7), $C_2H_7P^+$ (43), $C_2H_6P^+$ (32), $C_2H_4P^+$ (30), $C_2H_2P^+$ (28), $CH_3PH_2^+$ (4.7), CH_3PH^+ (9.6), CH_3P^+ (8.3), CH_2P^+ (21), $C_2H_5^+$ (7.7), and $C_2H_3^+$ (11).

Reaction of $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ with $CH_2{=}CHP(O)(OCHMe_2)_2$ Followed by $LiAlH_4$ Reduction. Reaction of 15.1 g (61.4 mmol) of $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ with 11.8 g (61.4 mmol) of $CH_2{=}CHP(O)(OCHMe_2)_2$ in the presence of ~ 0.25 g of potassium *tert*-butoxide in a total of 275 ml of tetrahydrofuran followed by reduction of the crude adduct with 5.0 g (132 mmol) of $LiAlH_4$ in a total of 250 ml of diethyl ether after a work-up procedure similar to that described above for the corresponding reaction with $(C_6H_5)_2PCH_2CH_2PH_2$ gave 3.26 g of a liquid, bp 175–178° (0.6–0.8 mm), shown by proton and phosphorus nmr spectra to be ~90% of unreacted $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ and ~10% of the secondary-tertiary-primary triphosphine $C_6H_5P(H)CH_2CH_2P(C_6H_5)CH_2CH_2PH_2$ and 6.41 g of a liquid, bp 180–215° (0.6–0.8 mm), shown by proton and phosphorus nmr spectra to be ~35% of unreacted $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ and ~65% of $C_6H_5P(H)CH_2CH_2P(C_6H_5)CH_2CH_2PH_2$. In making this analysis the ^{31}P nmr resonances at +20.3 (singlet), +46.7 (doublet, J = 210 Hz), and +127.3 ppm (triplet, $J = 190 \pm 10$ Hz) were assigned to the tertiary, secondary, and primary phosphorus atoms, respectively, of $C_6H_5P(H)CH_2CH_2P(C_6H_5)CH_2CH_2PH_2$. The proton nmr spectrum of $C_6H_5P(H)CH_2CH_2P(C_6H_5)CH_2CH_2PH_2$ appeared to exhibit a phenyl resonance at τ 3.0 (broad), a PH resonance centered at τ 6.02 (doublet of broad peaks, J = 202 Hz), a PH_2 resonance centered at τ 7.46 (doublet of triplets, J_D = 185, J_T = 6 Hz), and a CH_2 multiplet centered at τ 8.3. The relative amounts of $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ and $C_6H_5P(H)CH_2CH_2P(C_6H_5)CH_2CH_2PH_2$ in the product mixture were estimated from integration of the lower field halves of the PH and PH_2 doublets in the proton nmr spectrum. The yield of $C_6H_5P(H)CH_2CH_2P(C_6H_5)CH_2CH_2PH_2$ in the product mixture based on the $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ introduced was 24%.

Reaction of $C_6H_5P(H)CH_2CH_2PH_2$ with $CH_2{=}CHP(O)(OCHMe_2)_2$ Followed by $LiAlH_4$ Reduction. Reaction of 6.68 g (39 mmol) of $C_6H_5P(H)CH_2CH_2PH_2$ with 7.55 g (39 mmol) of $CH_2{=}CHP(O)(OCHMe_2)_2$ in the presence of ~0.15 g of potassium *tert*-butoxide in a total of 200 ml of tetrahydrofuran followed by the reduction of the crude adduct with 2.0 g (53 mmol) of $LiAlH_4$ in a total of 200 ml of diethyl ether after a work-up procedure similar to that described above for the corresponding reaction with $(C_6H_5)_2PCH_2CH_2PH_2$ gave 5.0 g of a liquid, boiling in the range 110–160° (0.4 mm), shown by its proton and ^{31}P nmr spectra to contain a mixture of the known compound[6] $C_6H_5P(CH_2CH_2PH_2)_2$ and unreacted $C_6H_5P(H)CH_2CH_2PH_2$.

Preparation of $C_6H_5P(CH_2CH_2PH_2)[CH_2CH_2P(CH_3)_2]$. A solution of 5.54 g (32.6 mmol) of $C_6H_5P(H)CH_2CH_2PH_2$ in 100 ml of tetrahydrofuran was treated with sufficient potassium *tert*-butoxide (~0.15 g) to produce a permanent yellow color. This solution was heated to boiling under reflux and then treated dropwise at the boiling point with a solution of 3.90 g (32.6 mmol) of dimethylvinylphosphine sulfide in 30 ml of tetrahydrofuran over a period of 2 hr. After heating for an additional 2 hr, solvent was removed at 0.1 mm. The resulting dirty brown oil was mixed with 100 ml of dioxane and 3.0 g (79 mmol) of $LiAlH_4$ and the mixture was boiled under reflux for 16 hr. After cooling to room temperature, the reaction mixture was hydrolyzed by the successive addition of 3 ml of water, 3 ml of 15% sodium hydroxide, and 9 ml of water. The precipitate was removed by filtration in a closed fritted flask under nitrogen and dioxane was removed from the filtrate at 0.1 mm. Vacuum distillation of the residue gave 5.74 g (61% yield) of liquid $C_6H_5P(CH_2CH_2PH_2)[CH_2CH_2P(CH_3)_2]$, bp 152° (1 mm).

Anal. Calcd for $C_{12}H_{21}P_3$: C, 55.8; H, 8.1; P, 36.0; mol wt, 258. Found: C, 56.0; H, 8.4; P, 35.8; mol wt, 248 (osmometer in benzene).

Infrared spectrum: ν(CH) bands at 3076 (w), 3059 (w), 2959 (m), 2930 (sh), 2900 (m), and 2818 (w); ν(PH) band at 2296 (m); other bands at 1487 (w), 1437 (m), 1423 (m), 1294 (w), 1279 (w), 1270 (vw, sh), 1179 (w), 1170 (sh), 1099 (w), 1080 (w), 1029 (w), 1002 (vw), 941 (m), 925 (w), 881 (vw), 839 (vw), 785 (vw), 743 (m), and 699 (s) cm^{-1}. Proton nmr spectrum: phenyl resonances at τ 2.60 (multiplet) and 2.82 (multiplet) of approximate relative intensities 2:3, PH_2 resonances at τ 7.31 (doublet of triplets, J_D = 188, J_T = 7 Hz), CH_2 resonances at τ 8.25 (broad multiplet) and 8.65 (broad multiplet) of approximately equal relative intensities, and CH_3 resonances at τ 9.14 (doublet; J = 2.7 Hz) and τ 9.16 (doublet, J = 2.8 Hz) of approximately equal relative intensities. Phosphorus nmr spectrum: resonances at +19.0 (singlet), +47.8 (doublet, J = 20 Hz), and +127.6 ppm (triplet of multiplets, J_T = 187, J_M = 8 Hz) assigned to the center tertiary phosphorus atom, the $P(CH_3)_2$ phosphorus atom, and the primary phosphorus atom, respectively. Mass spectrum (chamber temperature 100°, sample temperature 110°): $C_6H_5P(H)CH_2CH_2P(CH_3)_2^+$ (4), $C_6H_5P(H)CH_2CH_2PH_2^+$ and/or $C_6H_5P(H)P(CH_3)_2^+$ (44), $C_{10}H_{14}P^+$ (4), $C_9H_{13}P^+$ (5), $C_9H_{10}P^+$ (4), $C_6H_5P_2H_3^+$ (100), $C_8H_{11}P^+$ (5), $C_8H_{10}P^+$ (25), $C_8H_9P^+$ (13), $C_8H_8P^+$ (6), $C_8H_6P^+$ (6), $C_7H_9P^+$ (11), $C_7H_8P^+$ (5), $C_7H_7P^+$ (7), $C_7H_6P^+$ (14), $C_6H_7P^+$ (31), $C_6H_6P^+$ (130), $C_6H_5P^+$ (120), $C_6H_4P^+$ (47), $C_7H_{10}^+$ (9), $C_7H_9^+$ (8), $C_7H_8^+$ (5), $C_7H_7^+$ (11), $C_4H_4P^+$ (35), $C_6H_7^+$ (38), $C_6H_6^+$ (35), $C_6H_5^+$ (30), $C_5H_5^+$ and/or $P_2H_3^+$ (31), $C_2H_6P^+$ (22), $C_2H_4P^+$ (16), $C_2H_2P^+$ (40), $C_4H_3^+$ (19), $C_4H_2^+$ (9), CH_2P^+ (12), $C_3H_7^+$ (7), $C_3H_5^+$ (14), and $C_3H_3^+$ (27).

Results

Reactions of RPH_2 (R = phenyl, *n*-hexyl, and neopentyl) with $CH_2{=}CHP(O)(OCHMe_2)_2$ in a 1:1 mole ratio under base-catalyzed conditions result in selective addition of only one of the phosphorus-hydrogen bonds to the vinylphosphonate, as indicated by $LiAlH_4$ reductions of the adducts to give 31–43% yields of $RP(H)CH_2CH_2PH_2$. The phenyl derivative $C_6H_5P(H)CH_2CH_2PH_2$, was previously[5,6] obtained by a Michaelis-Arbusov reaction of $BrCH_2CH_2P(O)(OCHMe_2)_2$ with $C_6H_5P(OCHMe_2)_2$ followed by $LiAlH_4$ reduction.

The infrared spectra of $RP(H)CH_2CH_2PH_2$ exhibit the expected ν(PH) at ~2285 cm^{-1}. The phosphorus-31 nmr spectra exhibit the expected PH doublet and PH_2 triplet with coupling constants of ~200 Hz. The chemical shifts of the PH doublets vary more than those of the PH_2 triplets upon changing the alkyl group in the $RP(H)CH_2CH_2PH_2$ derivatives in accord with the closer proximity of the PH moiety than the PH_2 moiety to the alkyl group. The proton nmr spectra show doublets for the PH and PH_2 protons, but the higher half of each doublet is often obscured by the alkyl and/or PCH_2CH_2P resonances. Mass spectra show the expected molecular ions. Metastable ion analysis supports C_2H_4 elimination to give $RP_2H_3^+$ followed by PH_3 elimination to give RP^+. The elimination of hexene from the molecular ion of the *n*-hexyl derivative to give $H_2PCH_2CH_2PH_2^+$ is also indicated by an appropriate metastable ion.

An attempt was made to convert methylphosphine into $CH_3P(H)CH_2CH_2PH_2$ by a similar reaction sequence. However, the volatility of the gaseous methylphosphine prevented the stoichiometry from being controlled as closely as was possible with the liquid primary phosphines RPH_2 (R = phenyl, *n*-hexyl, and neopentyl). For this reason, the only liquid phosphorus-hydrogen compound obtained was $CH_3P(CH_2CH_2PH_2)_2$, a volatile air-sensitive liquid accompanied by pyrophoric by-products. It was identified by its ^{31}P and proton nmr spectra as well as its mass spectrum.

The molecular ion in the mass spectrum undergoes facile loss of a neutral PH_2 fragment as indicated by a strong metastable ion at *m/e* 108.7. The resulting ion $CH_3P(CH_2CH_2PH_2)CH_2CH_2^+$ is the most abundant ion in the mass spectrum by a factor of ~3 over the next most abundant ion. Loss of a neutral PH_3 fragment gives $CH_3P(C_2H_3)CH_2CH_2^+$ as indicated by a metastable ion at *m/e* 75.6. The predominant fragmentation of $CH_3P(CH_2CH_2PH_2)_2^+$ by successive losses of PH_2 and PH_3 fragments is unusual, since most polyphosphines with PCH_2CH_2P units eliminate C_2H_4 in the early stages of their fragmentation.[3,6] However, most of the other fragmentation processes for which unequivocal metastable ion evidence was obtained involve loss of C_2H_4 fragments.

Reactions of phenylphosphine with other vinylphosphorus compounds were investigated in order to determine which would give 1:1 adducts. Thus $CH_2{=}CHP(S)(CH_3)_2$ gives a good yield of $C_6H_5P(H)CH_2CH_2P(S)(CH_3)_2$. The proton nmr and infrared spectra provide unequivocal evidence for the secondary phosphine hydrogen, but this compound is too insoluble for a satisfactory ^{31}P nmr spectrum.

Desulfurization of $C_6H_5P(H)CH_2CH_2P(S)(CH_3)_2$ with $LiAlH_4$ in boiling dioxane gives $C_6H_5P(H)CH_2CH_2P(CH_3)_2$, which is more tractable than its phosphine sulfide precursor, since it is volatile enough to obtain a satisfactory mass spectrum and soluble enough to obtain ^{31}P and proton nmr spectra. We recently used similar desulfurization reactions for the preparation of methylated poly(tertiary phosphines).[7] The P-H bond in $C_6H_5P(H)CH_2CH_2P(CH_3)_2$ is indicated by the 2285-cm^{-1} band in the infrared spectrum and by the doublet PH resonance in the proton nmr spectrum. A proton nmr spectrum with the $(CH_3)_2P$ phosphorus decoupled shows that this phosphorus couples to the PH proton as well as to the methyl protons. In the ^{31}P nmr spectrum the lower half of the PH doublet overlaps with the $(CH_3)_2P$ phosphorus, but this overlap is in accord with the expected ^{31}P chemical shifts for these functionalities.[18] The mass spectrum exhibits the molecular ion which can fragment by loss of a methyl group or an ethylene bridge. Other observed metastable ions involve eliminations of PH or PH_2 fragments.

The reaction of $C_6H_5PH_2$ with diphenylvinylphosphine in the presence of potassium *tert*-butoxide was reported to give $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$.[3] At that time the reaction between $C_6H_5PH_2$ and $CH_2{=}CHP(C_6H_5)_2$ in a 1:1 mole ratio was also found to give only the same tri(tertiary phosphine). This reaction has now been investigated in greater detail using conditions successful in effecting 1:1 base-catalyzed additions of primary phosphines to other vinylphosphorus compounds. We also now know the properties of $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$, which we prepared by a different method and characterized in detail.[6] Our recent work confirms the earlier observations that the predominant product from $C_6H_5PH_2$ and $CH_2{=}CHP(C_6H_5)_2$ under base-catalyzed conditions, even in a 1:1 mole ratio, is the 1:2 adduct $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$. However, a small quantity of the 1:1 adduct $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$, identified by its proton nmr spectrum,[6] could be isolated from the filtrate after crystallization of the $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$. The yield of $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ was less than 20% of the yield of $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ suggesting that the base-catalyzed addition of primary phosphines to vinylphosphorus derivatives containing tricoordinate rather than tetracoordinate phosphorus atoms cannot be efficiently controlled to give the 1:1 adduct.

A more efficient method for converting $C_6H_5PH_2$ into $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ uses the addition of $C_6H_5PH_2$ to diphenylvinylphosphine sulfide in a 1:1 ratio to give $C_6H_5P(H)CH_2CH_2P(S)(C_6H_5)_2$, which undergoes desulfurization with $LiAlH_4$ in boiling dioxane to give $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ in 57% overall yield. The intermediate $C_6H_5P(H)CH_2CH_2P(S)(C_6H_5)_2$ could not be obtained crystalline but was identified by its elemental analyses, the presence of a ν(PH) band in its infrared spectrum, and a consistent proton nmr spectrum.

Similar 1:1 additions of phenylated diphosphines to $CH_2{=}CHP(O)(OCHMe_2)_2$ were investigated using $LiAlH_4$ reduction to convert the resulting $-CH_2CH_2P(O)(OR)_2$ group into the more tractable $-CH_2CH_2PH_2$ group as in the preparations of $RP(H)CH_2CH_2PH_2$. The products were separated by vacuum distillation after the $LiAlH_4$ reduction and base hydrolysis, but vacuum distillation could not separate completely the reduced adducts from unchanged diphosphine. The mixtures of products obtained in the liquid distillates were therefore analyzed by proton and phosphorus-31 nmr with the latter being particularly useful because of its ability to distinguish between tertiary, secondary, and primary phosphorus atoms.

A 1:1 addition of $(C_6H_5)_2PCH_2CH_2PH_2$ to $CH_2{=}CHP(O)(OCHMe_2)_2$ followed by $LiAlH_4$ reduction can give only $(C_6H_5)_2PCH_2CH_2P(H)CH_2CH_2PH_2$. The ^{31}P nmr spectrum of the higher boiling fraction is consistent with a mixture of unreacted $(C_6H_5)_2PCH_2CH_2PH_2$ and $(C_6H_5)_2PCH_2CH_2P(H)CH_2CH_2PH_2$. The presence of the secondary phosphine resonance as a doublet at +61.1 ppm is direct evidence for addition to only one of the two PH_2 hydrogens in $(C_6H_5)_2PCH_2CH_2PH_2$.

The similar 1:1 addition of $(CH_3)_2PCH_2CH_2PH_2$ to $CH_2{=}CHP(O)(OCHMe_2)_2$ followed by $LiAlH_4$ reduction gives $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2$, which can be separated in good yield in the pure state by vacuum distillation. The ^{31}P and proton nmr and mass spectra are consistent with the proposed formulation. The required starting material $(CH_3)_2PCH_2CH_2PH_2$ has not been reported in the literature but can be prepared by addition of $(CH_3)_2PH$ to $CH_2{=}CHP(O)(OCHMe_2)_2$ similar to the reported[4] preparation of $(C_6H_5)_2PCH_2CH_2PH_2$.

A 1:1 addition of the di(secondary phosphine) $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$ to $CH_2{=}CHP(O)(OCHMe_2)_2$ followed by $LiAlH_4$ reduction should give a different type of secondary-tertiary-primary triphosphine $C_6H_5P(H)CH_2CH_2P(C_6H_5)CH_2CH_2PH_2$. The ^{31}P nmr spectra of the volatile liquid products obtained from this reaction sequence exhibit two closely spaced secondary phosphorus doublets as well as a tertiary phosphorus singlet and a primary phosphorus triplet and thus are interpretable as mixtures of $C_6H_5P(H)CH_2CH_2P(C_6H_5)CH_2CH_2PH_2$ and unreacted $C_6H_5P(H)CH_2CH_2P(H)C_6H_5$.

The secondary-primary diphosphine $C_6H_5P(H)CH_2CH_2PH_2$ is a more interesting reagent since its 1:1 addition to $CH_2{=}CHP(O)(OCHMe_2)_2$ followed by $LiAlH_4$ reduction can involve either a primary phosphine hydrogen to give $C_6H_5P(H)CH_2CH_2P(H)CH_2CH_2PH_2$ or the secondary phosphine hydrogen to give $C_6H_5P(CH_2CH_2PH_2)_2$. The ^{31}P nmr spectrum of the volatile liquid product exhibits two distinct primary phosphine triplets, a weak secondary phosphine doublet, and a tertiary phosphine singlet and suggests a mixture of unreacted $C_6H_5P(H)CH_2CH_2PH_2$ and $C_6H_5P(CH_2CH_2PH_2)_2$ in a ~1:3 ratio.

The greater reactivity of the secondary phosphine hydrogen relative to the primary phosphine hydrogens in $C_6H_5P(H)CH_2CH_2PH_2$ allows the successive addition of the two phosphorus-hydrogen bonds in $C_6H_5PH_2$ to different vinylphosphorus compounds to prepare unsymmetrical organophosphorus derivatives of the type $C_6H_5P(CH_2$-

$CH_2PR^1R^2)(CH_2CH_2PR^3R^4)$. An example is the preparation of $C_6H_5P(CH_2CH_2PH_2)[CH_2CH_2P(CH_3)_2]$ from $C_6H_5PH_2$ through conversion to $C_6H_5P(H)CH_2CH_2PH_2$ followed by addition to $CH_2{=}CHP(S)(CH_3)_2$ and finally $LiAlH_4$ desulfurization. The ^{31}P nmr spectrum of $C_6H_5P(CH_2CH_2PH_2)[CH_2CH_2P(CH_3)_2]$ exhibits a doublet $(CH_3)_2P$ resonance (J = 20 Hz) suggesting coupling of this phosphorus atom with one of the other phosphorus atoms. The breadth and/or complexity of the other phosphorus resonances relative to a 20-Hz coupling does not allow an unequivocal decision regarding which phosphorus atom is involved in the coupling.

The mass spectrum of $C_6H_5P(CH_2CH_2PH_2)[CH_2CH_2P(CH_3)_2]$ does not exhibit a molecular ion. The highest *m/e* ions correspond to $C_6H_5P(H)CH_2CH_2P(CH_3)_2^+$ and $C_6H_5P(H)CH_2CH_2PH_2^+$ and suggest the reversal of the addition of phosphorus-hydrogen bonds to vinylphosphorus compounds in the mass spectrometer since $C_6H_5P(CH_2CH_2PH_2)[CH_2CH_2P(CH_3)_2]$ can arise from addition either of $C_6H_5P(H)CH_2CH_2PH_2$ to $CH_2{=}CHP(CH_3)_2$ or of $C_6H_5P(H)CH_2CH_2P(CH_3)_2$ to $CH_2{=}CHPH_2$. Further fragmentation involves processes typical of organophosphorus compounds including C_2H_4 elimination.

Discussion

The base-catalyzed addition of phosphorus-hydrogen bonds to vinylphosphorus compounds can be considered as a Michael addition[19] proceeding according to the following sequence.

$$R^1R^2PH + \text{base} \longrightarrow \text{base-}H^+ + R^1R^2P^- \qquad (1)$$

$$R^1R^2P^- + CH_2{=}CHPR^3R^4 \longrightarrow R^1R^2PCH_2CH^-PR^3R^4 \qquad (2)$$

$$R^1R^2CH_2CH^-PR^3R^4 + \text{base-}H^+ \longrightarrow R^1R^2PCH_2CH_2PR^3R^4 + \text{base} \qquad (3)$$

This is supported by the demonstration by Grim and coworkers[20] that $R^1R^2P^-$, formed from $R^1R^2PC_6H_5$ rather than R^1R^2PH, also undergoes similar additions to $CH_2{=}CHPR^3R^4$ to give reasonable yields of $R^1R^2PCH_2CH_2PR^3R^4$ after hydrolysis.

A similar sequence starting with RPH_2 (*i.e.*, R^1 = H and R^2 = R) would give $RP(H)CH_2CH^-PR^3R^4$ after the second step. This carbanion is in equilibrium with the tautomeric phosphide anion $RP^-CH_2CH_2PR^3R^4$. The equilibrium constant depends upon the relative acidities of the CH_2 hydrogens and the PH hydrogen. If these CH_2 hydrogens are relatively acidic, the carbanion will be favored over the tautomeric phosphide anion and will be a relatively poor nucleophile to undergo a second Michael addition. In this case it will be easy to stop the reaction at the $RP(H)CH_2CH_2R^3R^4$ stage. However, if the CH_2 hydrogens have a low acidity, the phosphide anion will be favored and will have a nucleophilicity roughly comparable to that of the original phosphide anion RPH^-. In this case $RP^-CH_2CH_2PR^3R^4$ will add readily to a second equivalent of the vinylphosphorus compound to give after protonation $RP(CH_2CH_2PR^3R^4)_2$ and it will be difficult to stop the reaction at the $RP(H)CH_2CH_2PR^3R^4$ stage.

Tetracoordinate phosphorus moieties including the $-P(S)R_2$ and $-P(O)(OR)_2$ groups used in this work are known[21] to "activate" an adjacent CH_2 group to make the hydrogens relatively acidic. The carbanion of the type $RP(H)CH_2CH^-P(S)R^1_2$ or $RP(H)CH_2CH^-P(O)(OR^1)_2$ thus will be greatly favored over the tautomeric phosphide anion $RP^-CH_2CH_2P(S)R^1_2$ or $RP^-CH_2CH_2P(O)(OR)_2$ and will be a relatively poor nucleophile. This accounts for the observation in this work that $CH_2{=}CHP(S)R^1_2$ and $CH_2{=}CHP(O)(OR^1)_2$ can readily be made to react with primary phosphines in a 1:1 mole ratio under base-catalyzed conditions. On the other hand, tricoordinate phosphorus moieties of the type $-PR_2$ (R = alkyl or aryl) preferentially form $RP^-CH_2CH_2PR^1_2$ rather than $RP(H)CH_2CH^-PR^1_2$. This accounts for the observation that the base-catalyzed addition of $C_6H_5PH_2$ to $CH_2{=}CHP(C_6H_5)_2$ gives almost exclusively the 1:2 adduct $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ even when the reactants are used in a 1:1 ratio. The nature of the vinylphosphorus compound is thus critical in determining the ease of stopping the reaction with primary phosphines at the 1:1 adduct.

The relative stability of appropriate anions also accounts for the observation that the secondary rather than a primary hydrogen in $C_6H_5P(H)CH_2CH_2PH_2$ first adds to vinylphosphorus compounds. The phosphide anion $C_6H_5P^-CH_2CH_2PH_2$ is stabilized over the isomeric phosphide anion $C_6H_5P(H)CH_2CH_2PH^-$ by the phenyl group directly bonded to the negatively charged phosphorus atom.

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