coefficients of the pure compounds at that wavelength and of the unknown concentrations of each of the three components. This set of 14 equations in 3 unknowns was solved by an IBM model 1800 computer by a method of least squares.[21] Results are given in the footnotes to Table I. Use of the method with known mixtures gave results accurate to better than 1%.

Registry No.—H-I, 14373-36-5; H-II, 21317-39-5; H-III, 21317-40-8; Br-I, 13025-90-6; Br-II, 21317-43-1; Br-III, 21317-42-0.

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[21] We are indebted to Professor D. H. Secrest for the suggestion of a generalized solution to this problem by matrix algebra.

Complex Metal Hydride Reduction of *t*-Alkynyl-1-phosphine Sulfides

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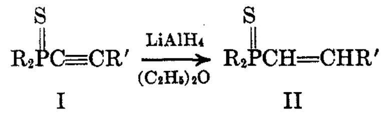
Reduction of a variety of diaryl- and dialkyl-1-alkynylphosphine sulfides to *trans*-β-substituted vinylphosphine sulfides employing lithium aluminum hydride is described. Support for a mechanistic path involving the β addition of a hydride ion is presented. Similar reduction of the corresponding alkynyl-1-phosphine oxides employing sodium borohydride is also described. A discussion of the 100-MHz proton nmr of α- and β-deuterated dimethyl-1-butenylphosphine sulfides is also included.

Desulfurization of *t*-phosphine sulfides has been accomplished with a variety of reagents including lithium aluminum hydride,[1a–d] iron,[1e] Raney nickel,[1a] sodium,[1f] and tributylphosphine.[1g] Reduction of α,β-unsaturated *t*-phosphine sulfides has not been investigated. We wish to report the results of our investigation into the use of complex metal hydrides as reagents in the reduction of *t*-α,β-unsaturated phosphine sulfides and oxides.

It was found that, when dimethyl-1-butynylphosphine sulfide (Ia, R = CH_3, R′ = C_2H_5) is treated with excess lithium aluminum hydride for 30 min in ether at room temperature, dimethyl-1-butenylphosphine sulfide (IIa, R = CH_3, R′ = C_2H_5) is obtained (eq 1).



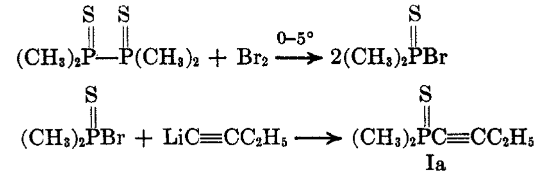
$$\underset{\text{I}}{R_2\overset{S}{\overset{\|}{P}}C\equiv CR'} \xrightarrow[(C_2H_5)_2O]{LiAlH_4} \underset{\text{II}}{R_2\overset{S}{\overset{\|}{P}}CH{=}CHR'} \qquad (1)$$

This is a direct analogy to the sodium borohydride reduction of acetylenic aromatic sulfide acids.[2]

The starting alkynyl sulfide (Ia) was prepared by bromination of tetramethylbiphosphine sulfide[3] followed by treatment with butynyllithium (Scheme I).

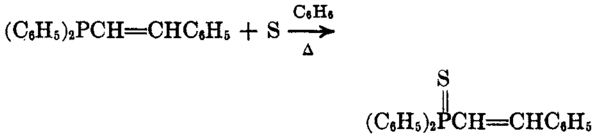
Comparison of the phosphorus–vinyl proton coupling constant in the proton nmr spectrum of IIa with the values for the same coupling in vinylphosphines and their oxides[4,5] leads to the tentative assignment of a *trans* configuration to this vinylphosphine sulfide. This assignment is supported by the fact that identical treatment of phenylethynyldiphenylphosphine sulfide[6] (Ib, R = R′ = C_6H_5) leads to the known *trans*-β-styryldiphenylphosphine sulfide[4] (IIb, R = R′ = C_6H_5). The heretofore unreported *cis*-β-styryldiphenylphosphine sulfide was prepared for comparison and found to be different as expected. Both the *cis*- and *trans*-β-styryldiphenylphosphine sulfides were independently prepared by treatment of the respective phosphine with sulfur in hot benzene[4,6] (eq 2). Compound Ib was obtained in the same fashion (eq 3).

SCHEME I

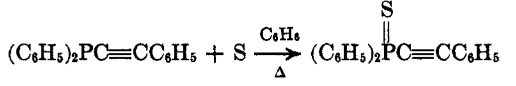


$$(CH_3)_2\overset{S}{\overset{\|}{P}}-\overset{S}{\overset{\|}{P}}(CH_3)_2 + Br_2 \xrightarrow{0\text{–}5^\circ} 2(CH_3)_2\overset{S}{\overset{\|}{P}}Br$$

$$(CH_3)_2\overset{S}{\overset{\|}{P}}Br + LiC\equiv CC_2H_5 \longrightarrow \underset{\text{Ia}}{(CH_3)_2\overset{S}{\overset{\|}{P}}C\equiv CC_2H_5}$$



$$(C_6H_5)_2PCH{=}CHC_6H_5 + S \xrightarrow[\Delta]{C_6H_6} (C_6H_5)_2\overset{S}{\overset{\|}{P}}CH{=}CHC_6H_5 \qquad (2)$$



$$(C_6H_5)_2PC\equiv CC_6H_5 + S \xrightarrow[\Delta]{C_6H_6} (C_6H_5)_2\overset{S}{\overset{\|}{P}}C\equiv CC_6H_5 \qquad (3)$$

No polymerization problem was encountered in the preparation of these unsaturated phosphine sulfides employing sulfurization.

Varying the substituents on either the phosphorus (R) or the alkynyl group (R′) in compounds I did not change the course of the reaction as is seen from Table I.

TABLE I

REDUCTION OF ALKYNYL-1-PHOSPHINE SULFIDES WITH LITHIUM ALUMINUM HYDRIDE

	I	II	Yield, %
a	$(CH_3)_2P(S)C\equiv CC_2H_5$	$(CH_3)_2P(S)CH{=}CHC_2H_5$	92
b	$(C_6H_5)_2P(S)C\equiv CC_6H_5$	$(C_6H_5)_2P(S)CH{=}CHC_6H_5$	100
c	$(C_6H_5)_2P(S)C\equiv CCH_3$	$(C_6H_5)_2P(S)CH{=}CHCH_3$	94.5
d	$(CH_3)_2P(S)C\equiv CC_6H_5$	$(CH_3)_2P(S)CH{=}CHC_6H_5$	85

Reduction of *t*-alkynyl-1-phosphine sulfides to the corresponding *trans*-vinylphosphine sulfides employing

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(1) (a) L. Horner, H. Hoffmann, and P. Beck, *Ber.*, **91**, 1583 (1958); (b) F. Hein, K. Issleib, and H. Rabold, *Z. Anorg. Allg. Chem.*, **287**, 208 (1956); *Chem. Abstr.*, **51**, 5619*i* (1957); (c) K. Issleib and A. Tzschach, *Ber.*, **92**, 704 (1959); (d) W. Kuchen and H. Buchwald, *Angew. Chem.*, **71**, 162 (1959); (e) L. Maier, *Helv. Chim. Acta*, **47**, 2137 (1964); (f) L. Horner, P. Beck, and H. Hoffmann, *Ber.*, **92**, 2088 (1959); (g) A. W. Parshall, *J. Inorg. Nucl. Chem.*, **14**, 291 (1960).

(2) F. Montanari, *Tetrahedron Letters*, No. 4, 18 (1960).

(3) L. Maier, *Chem. Ber.*, **94**, 3051 (1961); H. J. Harwood and K. A. Pollart, *J. Org. Chem.*, **28**, 3430 (1963).

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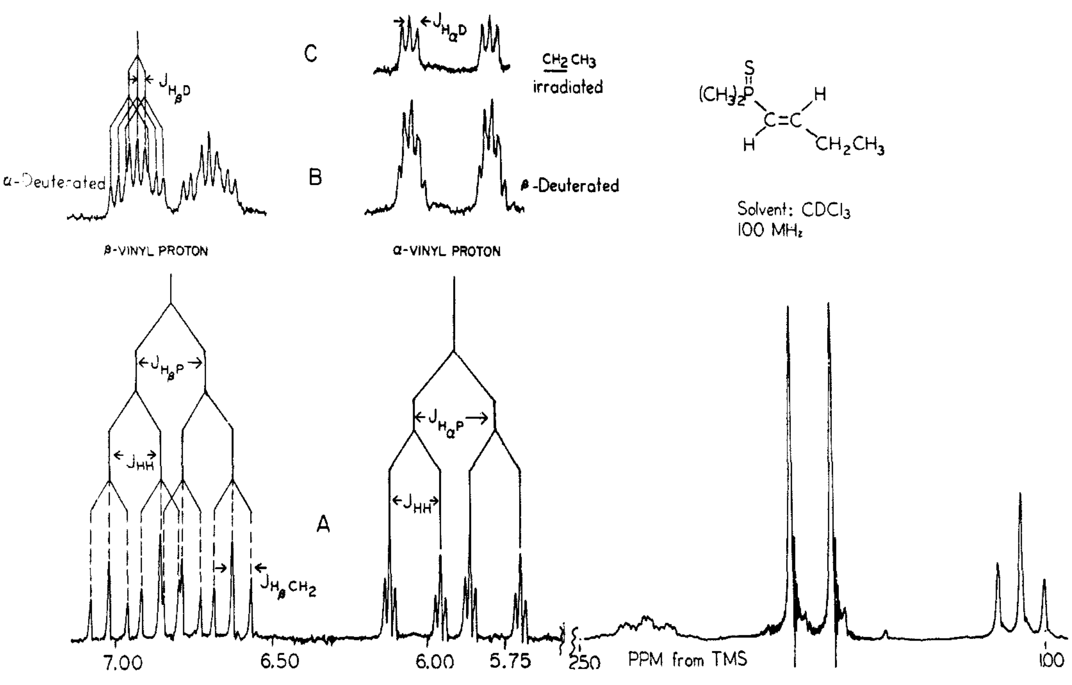
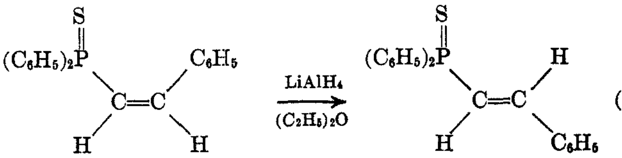


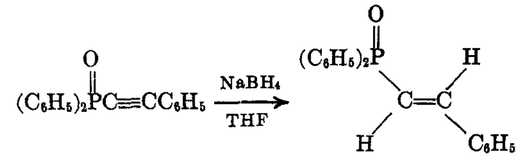
Figure 1.

lithium aluminum hydride seems to be generally applicable. It was shown that, under the conditions employed in this reduction, *cis*-β-styryldiphenylphosphine sulfide is isomerized to the *trans* isomer (eq 4).



(4)

In an attempt to extend this reaction to the phosphine oxides and phosphines themselves it was found that phenylethynyldiphenylphosphine (III) is unaffected by these conditions, whereas the corresponding oxide (IVb) gives saturated products which have not been completely characterized. It was found that sodium borohydride, in tetrahydrofuran, on the other hand, does convert IVb to *trans*-β-styryldiphenylphosphine oxide (Vb) (eq 5).



IVb Vb (5)

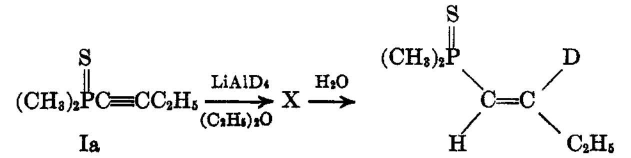
Interestingly, our results show that the corresponding sulfide Ib is unaffected by sodium borohydride even in boiling tetrahydrofuran. Similarly, the water-soluble dimethyl-1-butynylphosphine oxide (IVa, R = CH_3, R′ = C_2H_5) is reduced to the *trans* oxide (Va, R = CH_3, R′ = C_2H_5) with sodium borohydride in tetrahydrofuran (see Table II).

TABLE II

REDUCTION OF ALKYNYL-1-PHOSPHINE OXIDES WITH SODIUM BOROHYDRIDE

	IV	V	Yield, %
a	$(CH_3)_2P(O)C{\equiv}CC_2H_5$	$(CH_3)_2P(O)CH{=}CHC_2H_5$	47
b	$(C_6H_5)_2P(O)C{\equiv}CC_6H_5$	$(C_6H_5)_2P(O)CH{=}CHC_6H_5$	85.4

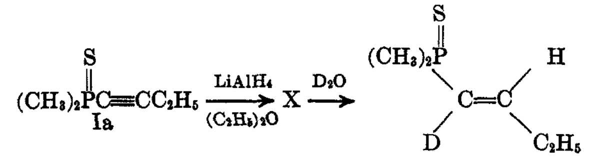
In an attempt to understand the mechanism of these reductions, Ia was reduced with lithium aluminum deuteride and the reaction mixture was treated with water (eq 6). Only the β-deuterated IIa was obtained.



Ia IIa (β-deuterated)

(6)

On the other hand, treatment of Ia with lithium aluminum hydride followed by treatment with D_2O led to the α-deuterated IIa (eq 7).



Ia IIa (α-deuterated) (7)

The 100-MHz proton nmr spectra of IIa, IIa (α-deuterated), and IIa (β-deuterated) are shown in Figure 1. The 100-MHz nmr spectrum of the sample (see Figure 1a) is in excellent accord with the proposed structure. The methyl protons of the ethyl group appear as a triplet ($J_{\mathrm{CH_3CH_2}}$ = 7.5 Hz) at δ 1.08 and the methylene protons appear as a complex multiplet at δ 1.75 due to their spin interactions with the methyl protons, the two olefinic hydrogens, and the ^{31}P nucleus. The downfield signals at δ 5.92 and 6.83 correspond to the vinyl hydrogens α and β to the thiophosphoryl group.

The α-vinyl hydrogen at δ 5.92 exhibits a twelve-line nmr pattern which is caused by the spin interactions of this hydrogen with the ^{31}P nucleus (J_{HP} = 22 Hz), the *trans* vinyl proton (J_{HH} = 16.25 Hz), and the allylic methylene hydrogens ($J_{\mathrm{HCH_2}}$ = 1.5 Hz). When the β-olefinic proton is replaced by deuterium, the

16.25-Hz *trans* hydrogen coupling is reduced to 2.5 Hz, and the nmr pattern for α-vinyl hydrogen appears as a doublet (J_{HP} = 22 Hz) of pseudoquintets (see Figure 1b), caused by an overlap of a triplet (J_{HD} = 2.5 Hz) of triplets (J_{HCH_2} = 1.5 Hz, seen in Figure 1a). The *trans* HD coupling of 2.5 Hz becomes clearly evident upon irradiation of methylene proton signals at δ 1.75, thereby removing the allylic coupling.

The β-vinyl proton resonance at δ 6.83 also exhibits a twelve-line pattern due to its spin interactions with the similar nuclei, as in the α-vinyl hydrogen. However, in this case the spin couplings between the *cis* ^{31}P nucleus (J_{PH} = 26 Hz) and the methylene protons (J_{HCH_2} = 6 Hz) are larger. Upon deuteration of the α-olefinic hydrogen, once again the large *trans* coupling of 16.25 Hz is reduced to a small magnitude of 2.5 Hz. The spectral lines for the β-vinyl hydrogen increase from twelve to eighteen (see Figure 1b) and the pattern corresponds to a doublet (J_{HP} = 26 Hz) of triplets (J_{HCH_2} = 6 Hz) of triplets (J_{HD} = 2.5 Hz) by first-order interpretation.

These facts indicate that the reducing agent adds a hydride ion to the β position in Michael fashion, *i.e.*, analogous to the reduction of cinnamate derivatives.[7-9]

At least 0.50 mol equiv of lithium aluminum hydride appear to be necessary for complete conversion to vinylphosphine sulfide. When the reaction was carried out using 0.358 mol equiv of the reducing agent, a mixture of the starting alkynylphosphine sulfide and the vinylphosphine sulfide product was obtained in the ratio of 45:55. When the reaction was carried out with 0.80 mol or more equiv of reducing agent, complete conversion of the alkynylphosphine sulfide into vinylphosphine sulfide occurred. These facts indicate that each molecule of $LiAlH_4$ reduces two molecules of alkynylphosphine sulfide by donating two hydrides, one to each of two alkynylphosphine sulfide molecules (eq 8).

$$2R_2P(S)C{\equiv}CR' + LiAlH_4 \longrightarrow 2[R_2P(S)C{=}CHR']^- + Li^+ + Al^-H_2 \quad (8)$$

Coordination of the aluminum or lithium with the sulfur of the polarized thiophosphoryl group is probably followed by or occurs in concert with addition of a hydride to the β-carbon to produce a variety of possible aluminum and/or lithium organometallics having the metal bonded to the α-carbon, the sulfur, or both. The exact structure of these intermediates awaits further work.

Experimental Section

All nmr spectra except that of IIa shown in the discussion were done at 60 MHz. Tetrahydrofuran was dried by storing over calcium hydride for 3–4 days and distilled from calcium hydride just before use.

Dimethyl-1-butynylphosphine Sulfide (Ia).—Approximately 10 ml of 1-butyne (Matheson) was condensed through an 8-mm glass U tube in a Dry Ice bath into a three-neck flask in a Dry Ice bath and under a nitrogen atmosphere. To the condensate was added 50 ml of dry tetrahydrofuran followed by 63 ml of 1.6 *M* butyllithium in hexane (Foote) over a 15-min period with stirring. The slurry was warmed to room temperature and immersed in an ice bath and a 100-ml dry tetrahydrofuran solution of 17.3 g of dimethylbromophosphine sulfide[3] was added over a 15-min period with stirring. The mixture was stirred at room temperature for 30 min and the solvent was stripped. Wet ether (150 ml) and water (100 ml) were added, the organic layer was washed once with water, dried ($MgSO_4$), and stripped to leave 14.45 g of dark liquid. The product was distilled (Claisen head) at 0.4 mm collecting one fraction, bp 77.5–81°. Redistillation (Claisen head) at 0.4 mm (discarding the small amount of forerun) yielded 10.73 g (73.5%) light yellow liquid, bp 80.5–82.0°. The ir spectrum ($CHCl_3$) showed prominent bands at 4.52 (intense, C≡C), 7.08, 7.60, 7.69, 7.76, 9.27 (P^+), 10.56, and 10.77 μ. The nmr spectrum ($CDCl_3$) displayed a multiplet at δ 2.17–2.68 for the allyl methylene (2 H) appearing as two quartets (*J* = 7 cps) at δ 2.39 and 2.45 (4 cps apart) with each peak finely split, the phosphorus methyls as a doublet at δ 1.95 (*J* = 14 cps, 6 H), and the terminal methyl as a slightly broadened triplet at δ 1.20 (*J* = 7 cps, 3 H).

Dimethylphenylethynylphosphine Sulfide (Id).—To a 50-ml dry tetrahydrofuran solution of 4.42 g of phenylacetylene in an ice bath was added 29 ml of 1.6 *M* butyllithium in hexane with stirring over a 10-min period. The mixture was cooled in a Dry Ice bath and a 30-ml dry tetrahydrofuran solution of 7.50 g of dimethylbromophosphine sulfide was added with stirring over a 20-min period. The mixture was allowed to warm to room temperature and stand overnight. The solvent was stripped, ether (150 ml) was added, and the organic solution was washed three times with water, dried ($MgSO_4$), and stripped to leave 8.30 g of dry yellow oil which solidified on cooling. Recrystallization from methanol produced 2.73 g of Id, mp 91–93° (lit.[10] 92.4–93.2°). The ir spectrum ($CHCl_3$) displayed bands at 4.58 (C≡C), 10.54, and 10.83 μ. The nmr spectrum ($CDCl_3$) exhibited an aromatic multiplet at δ 7.2–7.7 (5 H) and the phosphorus methyls as a doublet at δ 2.06 (*J* = 14 cps, 6 H).

Diphenyl-1-propynylphosphine Sulfide (Ic).—To a 100-ml dry tetrahydrofuran suspension of 9.20 g of propynyllithium (Foote) under nitrogen and in an ice bath was added a 60-ml dry tetrahydrofuran solution of 44.00 g of diphenylchlorophosphine (Aldrich) with stirring over a 2-hr period. The mixture was stirred 2 hr at room temperature and the solvent was stripped. Ether (250 ml) and water (100 ml) were added and the organic solution was washed three times with water, dried ($MgSO_4$), and stripped to leave 45.70 g of dark yellow liquid. The product was distilled (Claisen head) at 0.1 mm collecting 36.73 g of colorless liquid diphenyl-1-propynylphosphine,[11] bp 120–123° [lit.[11] 143° (0.1 mm)]. The ir spectrum ($CHCl_3$) exhibited significant absorptions at 4.55 (C≡C, strong), 6.74, 6.96 (phenyl P), 9.10, 9.64, and 9.71 μ. The nmr spectrum ($CDCl_3$) showed the aromatic protons as a complex multiple at δ 7.2–7.9 (10 H) and the methyl group as a close doublet at δ 2.02 (*J* = 1.8 cps, 3 H).

To 8.00 g of the above phosphine dissolved in 100 ml of benzene was added 1.30 g of sulfur powder and the mixture was brought just to reflux under nitrogen. The solution was stripped of solvent leaving 9.08 g of yellow oil which slowly crystallized (99%). Recrystallization twice from methanol produced Ic as a white solid, mp 91.5–94.0° (lit.[11] 88°). The ir spectrum ($CHCl_3$) displayed absorptions at 4.54 (C≡C, strong), 6.96 (phenyl P), 9.05 (P^+), and 9.51 μ (P=S). The nmr spectrum ($CDCl_3$) showed the aromatic protons as two multiplets at δ 7.75–8.25 and 7.35–7.70 (10 H) and the allyl methyl as a doublet (*J* = 4.5 cps) at δ 2.13 (3 H).

Dimethyl-1-butynylphosphine Oxide (IVa).—To 3.65 g of dimethyl-1-butynylphosphine sulfide (Ia) dissolved in 50 ml of methanol was added 50 ml of 3% hydrogen peroxide and the mixture was allowed to stand 2 days. The yellow solid was filtered out and excess sodium bisulfite was added to the filtrate. The filtrate was stripped to dryness (aspiration, hot water bath). The resulting salt was washed five times with 20-ml portions of ether, one 20-ml portion of 1:2 methanol–chloroform, and three 20-ml portions of chloroform. The combined organic solutions were stripped and the remaining liquid distilled (short path) at 0.20 mm collecting 1.99 g of IVa as a colorless liquid (61%), bp 75–76°. The ir spectrum ($CHCl_3$) showed bands at 4.55 (C≡C), 7.66, 7.72, 8.52 (P=O), 10.65, and 11.55 μ. The nmr spectrum ($CDCl_3$) exhibited the allyl methylene as two quartets (*J* = 7.5 cps each) at δ 2.33 and 2.40, each peak having fine splitting (2 H), the phosphorus methyls as a doublet (*J* = 13

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(7) F. A. Hochstein and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3484 (1948).

(8) R. Y. Uyeda and D. J. Cram, *J. Org. Chem.*, **30**, 2083 (1965).

(9) E. I. Snyder, *ibid.*, **32**, 3531 (1967).

(10) G. M. Bogolyubov and A. A. Petrov, *Zh. Obshch. Khim.*, **35**, 988 (1965); *Chem. Abstr.*, **63**, 9981*h* (1965).

(11) C. Charrier, M. P. Simonnin, W. Chodkiewicz, and P. Cadiot, *Compt. Rend.*, **258**, 1537 (1964).

cps) at δ 1.69 (6 H), and the terminal methyl group as a triplet (J = 7.5 cps) at δ 1.20 (3 H).

Reduction of Alkynylphosphine Sulfides. General Procedure.—To a 50–100-ml dry ether mixture of a 0.75–3.0 molar quantity of lithium aluminum hydride was added the alkynyl-1-phosphine sulfide (1–10 g), either in solution in ether or tetrahydrofuran or as the undissolved sulfide. The mixture was stirred at room temperature for 30–45 min under nitrogen, cooled in an ice bath and wet tetrahydrofuran (1:1 volume ratio) was added dropwise until the solid turned white. The mixture was filtered and the solvent was stripped from the filtrate to leave the crude alkenyl-1-phosphine sulfide. The product was purified by recrystallization or distillation. Products obtained are as follows.

Dimethyl-*trans*-1-butenylphosphine Sulfide (IIa).—A quantitative crude yield distilled (short path) twice, bp 70.5–73.0° (0.40 mm) (92%). The ir spectrum ($CHCl_3$) showed bands at 6.12 (C═C), 7.08, 7.76, 8.15 (broad), 10.23, and 10.6–10.8 μ (broad). The nmr spectrum displayed an ABMX pattern for the vinyl protons (2 H) with the α-proton appearing at δ 5.61 and 5.87 and the β-proton at δ 6.47 and 6.72. The α-proton was split into four lines by the phosphorus (J_{PH} = 25 cps) and finally into twelve lines by the allyl protons (J_{HH} = 1.5 cps). The β-proton of twelve lines showed coupling to phosphorus (J_{PH} = 22 cps) and to the allyl protons (J_{HH} = 5.5 cps). The allyl protons appeared as a complex multiplet at δ 1.93–2.50 (2 H). A doublet at δ 1.71 (J = 12.5 cps) could be seen for the protons on the phosphorus methyls (6 H) and a triplet at δ 1.05 (J = 7 cps) was assigned to the terminal methyl group (3 H).

Anal. Calcd for $C_6H_{13}PS$: C, 48.62; H, 8.84; P, 20.90; S, 21.64. Found: C, 48.06; H, 9.00; P, 20.72; S, 21.42.

Dimethyl-*trans*-β-styrylphosphine Sulfide (IId).—The crude yield was 85%, mp 124–126.5° (methanol). The ir spectrum ($CHCl_3$) showed bands at 6.18 (C═C), 7.77, 8.14 (broad), and 10.70 μ (broad). The nmr spectrum ($CDCl_3$) exhibited the aromatic protons as a multiplet at δ 7.25–7.70 covering part of the downfield half of the vinyl pattern, with the latter showing two peaks at δ 7.97 and 7.68 (6 H together). The upfield half of the vinyl ABX pattern appeared at δ 6.48 and 6.76 and showed coupling to phosphorus (J_{PH} = 23.5 cps, 1 H). The phosphorus methyls appeared as a doublet at δ 1.86 (J = 13 cps, 6 H).

Anal. Calcd for $C_{10}H_{13}PS$: C, 61.20; H, 6.68; P, 15.78; S, 16.34. Found: C, 61.09; H, 6.73; P, 15.83; S, 16.32.

Diphenyl-*trans*-1-propenylphosphine Sulfide (IIc).—The crude yield was 94.5%, mp 77.5–79.5° (methanol). The ir spectrum ($CHCl_3$) displayed absorptions at 6.11 (C═C), 6.95 (phenyl-P), 9.03 (P^+), and 10.35 μ. The nmr spectrum ($CDCl_3$) showed the aromatic protons as two multiplets at δ 7.3–7.65 and 7.65–8.1, covering the downfield most peaks of the vinyl ABMX pattern (12 H together). The α-proton appeared at δ 6.55 and 6.28 and was coupled to phosphorus (J_{PH} = 24 cps) and the allyl protons ($J \approx 1.0$ cps). The β-proton appeared at δ 7.05 and 6.78 and showed phosphorus coupling (J_{PH} = 22.5 cps) and coupling to the allyl protons (J = 6 cps). The allyl methyl group appeared as two close multiplets at δ 1.95–2.10 (3 H).

Anal. Calcd for $C_{15}H_{15}PS$: C, 69.74; H, 5.85; P, 11.99; S, 12.41. Found: C, 70.00; H, 5.83; P, 11.88; S, 12.48.

Diphenyl-*trans*-β-styrylphosphine Sulfide (IIb).[6]—The crude yield was quantitative, mp 105.5–108° (ethanol). The ir spectrum ($CHCl_3$) showed bands at 6.21 (C═C), 6.96 (phenyl-P), 9.04 (P^+), 10.21, and 11.79 μ. The nmr spectrum ($CDCl_3$) exhibited the aromatic protons at δ 7.25–8.1 as a multiplet covering the downfield five of the eight lines in the ABX vinyl pattern. The α-proton appeared at δ 6.81 and 7.08 and showed coupling to phosphorus (J_{PH} = 21 cps).

Dimethyl-*trans*-1-butenylphosphine Oxide (Va).—To 0.5 g of sodium borohydride in 30 ml of dry tetrahydrofuran was added a 10-ml dry tetrahydrofuran solution of 0.50 g of IVa and the mixture was stirred under nitrogen at room temperature for 5.5 hr. To the mixture was slowly added 3.5 g of acetic acid in 15 ml of tetrahydrofuran and the solution was allowed to stand overnight. The mixture was stripped to dryness and the resulting gummy solid was washed three times with chloroform. After evaporation of the solvent the residue was distilled (short path) at 0.15 mm, bp 59°, to give 0.24 g of Va (47%) as a colorless liquid. The ir spectrum ($CHCl_3$) displayed significant bands at 6.12 (C═C), 7.68, 8.66 (P═O), 10.69, and 11.60 μ. The nmr spectrum ($CDCl_3$) showed an ABMX vinyl pattern (2 H) with the α-proton appearing at δ 5.71 and 6.00 and the β-proton at δ 6.65 and 6.94. The α-proton showed coupling to the phosphorus (J_{PH} = 25.5 cps) and to the allyl protons (J_{HH} = 1.5 cps). The β-proton displayed the same type coupling with different values (J_{PH} = 22 cps, J_{HH} = 6 cps). The allyl protons appeared as a multiplet at δ 2.0–2.6 (2 H), the phosphorus methyls as a doublet (J = 13 cps) at δ 1.54 (6 H), and the terminal methyl group as a triplet (J = 7 cps) at δ 1.10 (3 H).

The same compound could be obtained by oxidation of IIa using the same procedure as described for the preparation of IVa.

Diphenyl-*trans*-β-styrylphosphine Oxide (Vb).[6]—A quantity of 1.00 g of IVb[11] was reduced with 0.5 g of sodium borohydride as described for Va. The reaction mixture was filtered, the solvent was stripped, and the residue was taken up in ether. The solution was washed with water and sodium bicarbonate solution dried ($MgSO_4$), and stripped to leave 0.86 g of white solid Vb (85.4%), mp 163–165° (ethanol). The ir spectrum ($CHCl_3$) showed bands at 6.21 (C═C), 6.96 (phenyl P), 8.50 (P═O), 8.90, and 9.04 μ. The nmr spectrum ($CDCl_3$) exhibited an aromatic multiplet at δ 7.15–8.0 covering the five downfield peaks of the vinyl ABX pattern. The α-proton appeared at δ 6.70 and 6.98 and showed phosphorus coupling (J_{PH} = 22 cps).

Diphenyl-*cis*-β-styrylphosphine Sulfide.—To 3.36 g of diphenyl-*cis*-β-styrylphosphine[6] dissolved in 50 ml of benzene was added 0.40 g of sulfur and the mixture refluxed 20 min. The solution was cooled some and the solvent was stripped to leave 3.72 g of light yellow oil which slowly crystallized (quantitative yield), mp 110–112° (ethanol). The ir spectrum ($CHCl_3$) exhibited bands at 6.26 (C═C), 6.96 (phenyl P), 9.07 (P^+), and 11.91 μ. The nmr spectrum ($CDCl_3$) displayed an aromatic multiplet at δ 6.95–8.15 covering the downfield half of the vinyl ABX pattern (16 H). The α-proton appeared at δ 6.30 and 6.52 (1 H) and showed phosphorus coupling (J_{PH} = 18 cps).

Anal. Calcd for $C_{20}H_{17}PS$: C, 74.97; H, 5.35; P, 9.67; S, 10.01. Found: C, 74.95; H, 5.30; P, 9.46; S, 10.01.

Dimethyl-2-deuterio-*trans*-1-butenylphosphine Sulfide.—A quantity of 1.00 g of Ia was reduced with 0.30 g of lithium aluminum deuteride using the general procedure. The product was distilled (short path) at 0.45 mm, bp 72–72.5°, collecting 0.78 g of colorless liquid (76.5%). The nmr spectrum ($CDCl_3$) displayed the α-vinyl hydrogen at δ 5.97 (1 H) and showed coupling to phosphorus (J_{PH} = 25.5 cps). Coupling to the β-deuteron and the allyl hydrogens reduced the doublet to two close multiplets. The allyl hydrogens appeared as a multiplet at δ 2.00–2.60 (2 H), the phosphorus methyls as a doublet (J = 13 cps) at δ 1.76 (6 H), and the terminal methyl group as a triplet (J = 7.5 cps) at δ 1.09 (3 H).

Dimethyl-1-deuterio-*trans*-1-butenylphosphine Sulfide.—A quantity of 1.00 g of Ia was reduced with 0.50 g of lithium aluminum hydride using the general procedure except that deuterium oxide was used in place of water at the end of the reaction. The product was distilled (short path) at 0.35 mm, bp 68°, collecting 0.61 g of colorless liquid (60%). The nmr spectrum ($CDCl_3$) exhibited the β-hydrogen as two broad multiplets at δ 6.43–6.82 and 6.82–7.20 (1 H) with phosphorus coupling of 23 cps. The allyl hydrogens appeared as a multiplet at δ 2.00–2.60 (2 H), the phosphorus methyls as a doublet (J = 13 cps) at δ 1.77 (6 H), and the terminal methyl as a triplet (J = 7.5 cps) at δ 1.10 (3 H).

Registry No.—Ia, 21299-42-3; Ic, 6104-31-0; Id, 2633-26-3; IIa, 21298-92-0; IIb, 3582-83-0; IIc, 21298-94-2; IId, 21298-95-3; IVa, 21299-44-5; Va, 21298-96-4; Vb, 3582-82-9; diphenyl-*cis*-β-styrylphosphine sulfide, 21298-89-5; dimethyl-2-deuterio-*trans*-1-butenylphosphine sulfide, 21298-90-8; dimethyl-1-deuterio-*trans*-1-butenylphosphine sulfide, 21298-91-9.

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