Synthesis of P,P,P',P'-Tetraalkylated 1,4-Diphosphoniacyclohexadiene-2,5 Salts

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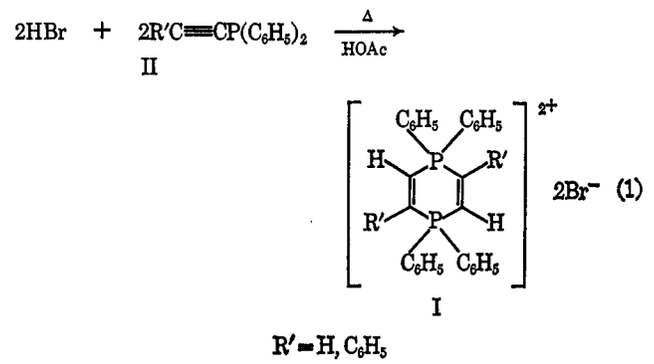
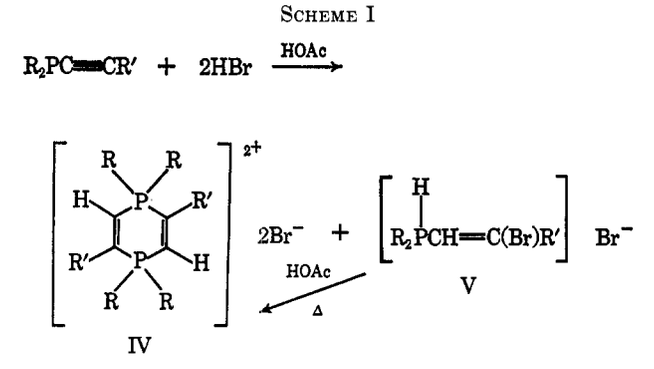
The preparation of the new class of phosphorus alkylated 1,4-diphosphoniacyclohexadiene-2,5 salts and β-halovinylphosphines from dialkyl-1-alkynylphosphines is described. Implications toward possible reaction sequences are discussed.

The preparation of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexadiene-2,5 dibromides (I) by the reaction of diphenyl-1-alkynylphosphines (II) with hydrogen bromide in hot glacial acetic acid was reported from this laboratory in 1967 (eq 1).[3,4]



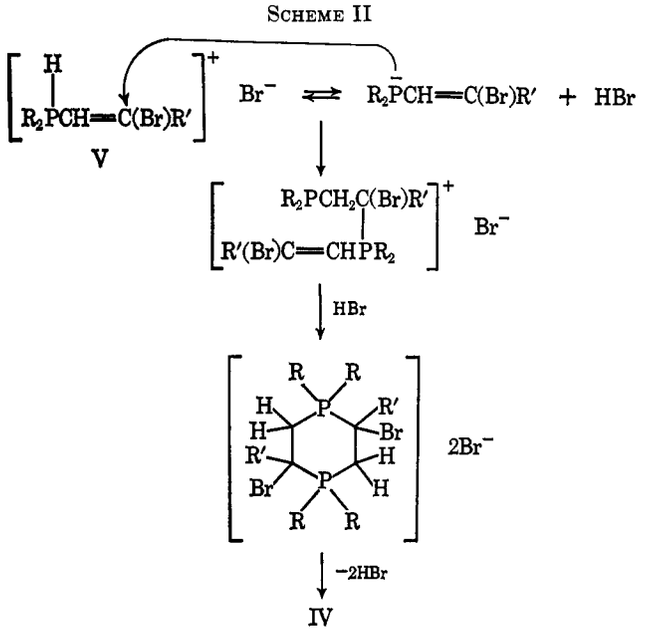
This synthesis was limited to the P-phenylated "diphosphoniapyrazine" salts (I) owing to the difficulty in obtaining dialkyl-1-alkynylphosphines (III).[5] This difficulty has now been overcome.[6] Treatment of the dialkyl-1-alkynylphosphines (III) with hydrogen bromide in boiling glacial acetic acid did not lead to the tetraalkylated salts (IV) in most cases, and in the one case in which the salt was obtained, the yield was less than 10%. At room temperature or lower, however, the same reagents do give rise to IV and β-bromovinylphosphine hydrobromides (V) (Scheme I). The major product under these conditions is usually V. Conversion of V into IV occurs readily in boiling glacial acetic acid (Scheme I).

SCHEME I



A series of acid-catalyzed Michael additions of phosphines to β-bromovinylphosphine hydrobromides and phosphonium salts followed by elimination of hydrogen bromide may explain the formation of IV from V (Scheme II).

SCHEME II



Although treatment of the isolated V with hot glacial acetic acid leads to IV, formation of IV can occur without the intermediacy of β-bromovinylphosphines by a series of acid-catalyzed Michael additions to alkynylphosphines (Scheme III).

This is shown by the fact that the dichlorides of IV are formed in higher yields than are the corresponding dibromides by the use of hydrogen chloride gas instead of hydrogen bromide. Further support for this explanation is found in the fact that usually no chlorovinylphosphines or their hydrochlorides are isolated under these conditions. These data are summarized in Table I.

It seems that there is competition between the halide ion and phosphine in the acid-catalyzed addition step to the alkynylphosphine. The bromide ion competes effectively with the phosphines and leads to some bromovinylphosphine. The chloride ion, on the other hand, is not so effective in the competitive nucleophilic addition. Relative acidity of the acid is apparently not so important as the nucleophilicity of its conjugate

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(3) A. M. Aguiar, K. C. Hansen, and G. S. Reddy, *J. Amer. Chem. Soc.*, **89**, 3067 (1967).
(4) A. M. Aguiar and K. C. Hansen, *ibid*, **89**, 4235 (1967).
(5) W. E. Davidsohn and M. C. Henry, *Chem. Rev.*, **67**, 73 (1967).
(6) A. M. Aguiar, J. R. S. Irelan, C. J. Morrow, J. P. John, and G. W. Prejean, *J. Org. Chem.*, **34**, 2684 (1969).

TABLE I

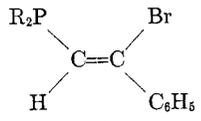
				IV			V	
R	R′	X⁻	Temp, °C	Yield, %	Mp (dec), °C	Picrate mp (dec), °C	Yield, %	Mp (dec), °C
CH_3	C_2H_5	Br	25	0	...	...	50	149–151
CH_3	C_2H_5	Br	125	35[a]	370–372	246–248	0	...
CH_3	C_2H_5	Cl	25	32	365–370	246–248[c]	0	...
CH_3	C_6H_5	Br	125	0	...	...	0	...
CH_3	C_6H_5	Br	25	51[b]	327–328[b]	273[c]	38	146.5–147.5
CH_3	C_6H_5	Cl	25	45	314–316	273[c]	0	...
C_2H_5	CH_3	Cl	25	20	305–307	245–247	0	...
C_2H_5	CH_3	Br	125	7.6[b]	318–320	245–247	76	...
C_2H_5	C_6H_5	Br	125	10	279–281	265–266[c]	40	150–152
C_2H_5	C_6H_5	Br	125	20[d]	279–281	265–266	0	...
C_2H_5	C_6H_5	Cl	25	30	285–287	265–266[c]	0	...
$(CH_3)_2CH$	$(CH_2)_2CH_3$	Cl	25	30	280–283	200–202	0	...
$(CH_3)_2CH$	H	Cl	25	38	285–287	200–202	0	...
$(CH_3)_2CH$	C_6H_5	Cl	25	7.2	270–273	263–265	0	...
$C_6H_5CH_2$	CH_3	Cl	25	45[b]	260–262	242–244	77	...

[a] Retreatment of isolated V with HX in glacial acetic acid. [b] Obtained by boiling V in glacial acetic acid. [c] Mixture melting point undepressed. [d] Added $R_2PC{\equiv}CR'$ to refluxing solution of HBr in HAc.

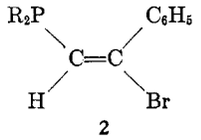
base. As predicted by this mechanistic explanation, hydrogen iodide seems to give only the β-iodovinylphosphine hydriodides, while trifluoroacetic acid leads to ring formation with little difficulty.

The conclusion that V is a bromovinylphosphine hydrobromide is based upon elemental analysis (where R = C_2H_5, R′ = C_6H_5), the presence of a P–H band of high intensity at 2260 cm^{-1}, immediate formation of a precipitate upon treatment with aqueous silver nitrate, and failure to form a picrate when treated with sodium picrate. Conversion of V to VI by pyridine further supports this conclusion. No 2260 cm^{-1} band was found for VI.

There are four stereochemical possibilities for the structure of VI (**1**, **2**, **3**, and **4**).



1



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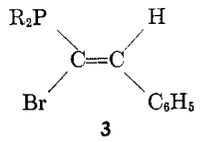

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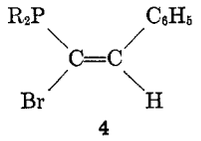


4

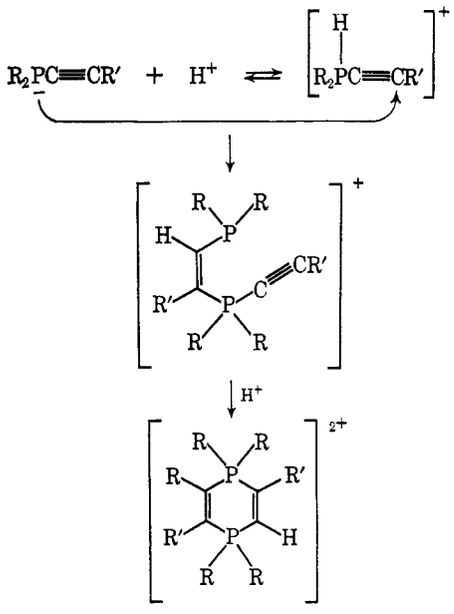
That the intermediate VI is not an α-bromovinylphosphine (**3** and **4**) is supported by the results obtained when diphenyl-1-butynylphosphine was treated with dry HBr in benzene (eq 2).

$$(C_6H_5)_2PC{\equiv}CC_2H_5 + HBr \xrightarrow{C_6H_6} (C_6H_5)_2PCH{=}C(Br)C_2H_5 \quad (2)$$

In this reaction, HBr added once across the triple bond to yield a β-bromovinylphosphine, evidenced by the lack of a coupling constant between the vinyl proton and the methylene of the ethyl group as well as the simplicity of the vinyl proton signal (see Experimental Section for spectrum).

The stereochemistry of VI is suspected to be either a mixture of **1** and **2** or only **1** rather than **2**, for there is reason to expect equilibration and **1** would be expected to be more stable, but this awaits further work.

SCHEME III



Experimental Section

All reactions, from the introduction of acetic acid until the removal of solvent, were performed under nitrogen. The hydrogen chloride and hydrogen bromide were used directly from the bottle (Matheson Chemical Co.). The acetic acid was deaerated by bubbling in nitrogen for 10–20 min. Picrates were formed by metathetical reaction between a methanolic solution of the phosphonium salt and a methanolic solution of sodium picrate.

P,P,P′,P′-Tetraalkyl-1,4-diphosphoniacyclohexadiene-2,5 Salts. General Procedure.—To 50 ml of deaerated acetic acid was added a 10-ml acetic acid solution of 2–5 g of dialkyl-1-alkynylphosphine, and then dry hydrohalic acid was bubbled in at room temperature or with the flask immersed in an ice bath. Slow addition of HX was carried out for 30–60 min and the mixture was allowed to stand under nitrogen at room temperature for 3–5 days or the solution was refluxed for 2–4 hr. The acetic acid was then removed in each case by heating with a hot (60–80°) water bath and stirring (magnetic) under aspirator pressure. The last traces of acetic acid were removed *in vacuo* at 60–80° (1.0–0.1 mm) for 1–3 hr. The resulting gum was triturated with ether, and acetone was added. If the salt precipitated, it was filtered out. If no solid formed, the acetone solution was cooled to −20° until precipitation occurred. The resulting diphosphonium salt was normally recrystallized from methanol–ethyl acetate. If the intermediate V was isolated (as indicated by

spectra), it was dissolved in 50 ml of acetic acid, refluxed for 4–6 hr, and worked up on the same manner as before.

Frequently, the salts were hygroscopic or associated with small amounts of solvents, rendering purification difficult. The picrate salts, which could be obtained pure, were thus formed, and microanalyses were performed on these.

Characteristics of the salts are as follows.

IV, R = CH_3, R′ = CH_2CH_3, X = Br.—The ir spectrum (KBr) showed bands at 1705, 1600 (C=C), 1465, and 1410 cm^{-1}. The nmr spectrum in trifluoroacetic acid (TFA) presented a pseudotriplet[3,4] at δ 7.62 ($J \approx 26$ cps) for the vinyl protons (2 H), a multiplet at δ 2.6–3.15 for the allyl protons (4 H), two sharp peaks at δ 2.32 and 2.56 above a broad center peak at δ 2.45 representing the methyl groups on phosphorus (12 H), and a triplet at δ 1.47 (J = 7 cps) for the terminal methyl groups (6 H).

IV, R = CH_3, R′ = CH_2CH_3, X = Cl.—The nmr spectrum (TFA) of the dichloride is like that of the dibromide but displaying the vinyl pseudotriplet at δ 7.59 (slightly upfield).

IV, R = CH_3, R′ = CH_2CH_3, X = Picrate.

Anal. Calcd for $C_{24}H_{27}N_6O_{14}P_2$: C, 42.00; H, 4.08; N, 12.24; P, 9.03. Found: C, 41.88; H, 4.12; N, 12.16; P, 9.13.

IV, R = CH_3, R′ = C_6H_5, X = Br.—The ir spectrum (KBr) showed significant bands at 1560 (C=C), 1495, 1447, and 1302 cm^{-1}. The nmr spectrum (TFA) exhibited a broadened aromatic singlet at δ 7.70 above the vinyl pseudotriplet at δ 7.89 (J = 26 cps, 12 H together) and the methyl groups on phosphorus as two sharp peaks at δ 2.49 and 2.74 above a broad center peak at δ 2.60 (12 H).

IV, R = CH_3, R′ = C_6H_5, X = Cl.—The ir spectrum (KBr) displayed significant bands at 1630, 1550 (C=C), 1480, 1435, 1403, and 1285 cm^{-1}. The nmr spectrum (TFA) showed the same spectrum as the dibromide but displayed the aromatic protons as a multiplet at δ 7.41–8.32 above the vinyl pseudotriplet at δ 7.82 (J = 26 cps). The methyl groups on phosphorus show the same pattern at the same shift as the dibromide.

IV, R = CH_3, R′ = C_6H_5, X = Picrate.

Anal. Calcd for $C_{32}H_{28}N_6O_{14}P_2$: C, 49.11; H, 3.61; N, 10.74. Found: C, 48.41; H, 3.80; N, 10.33.

IV, R = CH_2CH_3, R′ = CH_3, X = Br.—The nmr spectrum (TFA) displayed the vinyl pseudotriplet at δ 7.90 (J = 25 cps, 2 H), the methylenes on phosphorus and the allyl methyl groups as a complex multiplet at δ 2.5–3.2 (14 H), and the methyls of the ethyl groups as two triplets at δ 1.60 and 1.23 (J = 7.5 cps each) above a broad region at δ 1.05–1.80 (12 H).

IV, R = CH_2CH_3, R′ = CH_3, X = Cl.—The ir spectrum (KBr) showed bands at 1470 (C=C), 1410, 1310, 1250, and 1110 cm^{-1}. The nmr spectrum (TFA) showed the same spectrum as the dibromide but displayed the vinyl pseudotriplet at δ 7.69 (J = 25 cps).

IV, R = CH_2CH_3, R′ = CH_3, X = Picrate.

Anal. Calcd for $C_{26}H_{32}N_6O_{14}P_2$: C, 43.71; H, 4.51; N, 11.76; P, 8.67. Found: C, 43.78; H, 4.39; N, 12.09; P, 8.39.

IV, R = CH_2CH_3, R′ = C_6H_5, X = Br.—The ir spectrum (KBr) showed bands at 1595 (C=C) 1481, 1445, 1400, 1285, and 1262 cm^{-1}. The nmr spectrum (TFA) exhibited a broad aromatic multiplet at δ 7.5–7.95 above the upfield half of the vinyl pseudotriplet at δ 8.12 (J = 25 cps, 12 H together), a broad multiplet at δ 2.3–3.5 for the methylenes next to phosphorus (8 H), and a broad multiplet at δ 1.1–1.9 which contains two triplets at δ 1.35 and 1.71 (J = 7.5 cps each, 12 H).

IV, R = CH_2CH_3, R′ = C_6H_5, X = Cl.—The ir spectrum (KBr) displayed bands at 1610 (C=C), 1500, 1450, 1392, 1295, and 1281 cm^{-1}. The nmr spectrum (TFA) showed the same spectrum as the dibromide, except that the vinyl pseudotriplet appeared upfield at δ 7.70 (J = 25 cps).

Anal. Calcd for $C_{24}H_{32}Cl_2P_2$: C, 63.58; H, 7.11; Cl, 15.64; P, 13.66. Found: C, 63.35; H, 7.11; Cl, 15.69; P, 13.12.

IV, R = CH_2CH_3, R′ = C_6H_5, X = Picrate.

Anal. Calcd for $C_{36}H_{36}N_6O_{14}P_2$: C, 51.56; H, 4.33; N, 10.02; P, 7.39. Found: C, 51.64; H, 3.63; N, 10.24; P, 7.62.

IV, R = $(CH_3)_2CH$, R′ = $(CH_2)_2CH_3$, X = Cl.—The nmr spectrum (TFA) exhibited the vinyl pseudotriplet at δ 7.61 (J = 25 cps, 2 H), the central hydrogens in the isopropyl groups with the allyl methylenes as two broad multiplets δ 2.6–3.8 (8 H), and the remainder of the hydrogens in a multipeak region at δ 1.0–2.3 (34 H).

IV, R = $(CH_3)_2CH$, R′ = $(CH_2)_2CH_3$, X = Picrate.

Anal. Calcd for $C_{34}H_{48}N_6O_{14}P_2$: C, 49.40; H, 5.85; N, 10.17; P, 7.49. Found: C, 49.07; H, 5.76; N, 10.17; P, 7.64.

IV, R = $(CH_3)_2CH$, R′ = H, X = Cl.—The ir spectrum (KBr) showed bands at 1453 (C=C), 1260, 1253, and 1042 cm^{-1}. The nmr spectrum (TFA) displayed the vinyl pseudotriplet at δ 8.13 (J = 26 cps, 4 H), the central hydrogens in the isopropyl groups as a broad multiplet at δ 2.83–3.50 (4 H), and the methyl groups as four sharp peaks at δ 1.20, 1.31, 1.53, and 1.65 above a broad multiplet at δ 1.10–1.75 (12 H).

IV, R = $(CH_3)_2CH$, R′ = H, X, = Picrate.

Anal. Calcd for $C_{28}H_{36}N_6O_{14}P_2$: C, 45.29; H, 4.89; N, 11.32; P, 8.34. Found: C, 45.28; H, 4.93; N, 12.19; P, 8.21.

IV, R = $(CH_3)_2CH$, R′ = C_6H_5, X = Cl.—The ir spectrum (KBr) displayed bands at 1610 (C=C), 1450, 1395, 1295, and 1280 cm^{-1}. The nmr spectrum (TFA) exhibited the vinyl pseudotriplet at δ 7.89 (J = 24 cps) beneath an aromatic multiplet at δ 7.5–8.0 (6 H together), the central hydrogen in the isopropyl groups as a multiplet at δ 3.2–3.9 (4 H), and the methyl groups as a group of eight broadened peaks at δ 1.17–1.97 (12 H).

IV, R = $(CH_3)_2CH$, R′ = C_6H_5, X = Picrate.

Anal. Calcd for $C_{40}H_{44}N_6O_{14}P_2$: C, 53.70; H, 4.96; N, 9.39; P, 6.94. Found: C, 53.76; H, 4.82; N, 9.32; P, 7.06.

IV, R = $C_6H_5CH_2$, R′ = CH_3, X = Cl.—The ir spectrum (KBr) showed bands at 1620, 1590, 1490 (C=C), 1450, and 1270 cm^{-1}. The nmr spectrum (TFA) showed two close aromatic multiplets at δ 6.95–7.65 covering all but the downfield peak at δ 7.87 of the vinyl pseudotriplet (22 H together), a broad multiplet at δ 3.6–4.1 for the benzyl hydrogens (8 H), and a multiplet at δ 2.45–2.70 for the allyl methyls showing two rounded peaks at δ 2.54 and 2.72 (6 H).

IV, R = $C_6H_5CH_2$, R′ = CH_3, X = Picrate.

Anal. Calcd for $C_{46}H_{40}N_6O_{14}P_2$: C, 57.30; H, 4.15; N, 8.73; P, 6.44. Found: C, 57.13; H, 4.15; N, 8.56; P, 6.34.

V, R = CH_3, R′ = CH_2CH_3, X = Br.—The ir spectrum ($CHCl_3$) displayed bands at 2435 (P-H), 1600 (C=C), and 1355 cm^{-1}. The nmr spectrum (TFA) exhibited a crude vinyl doublet at δ 6.52 (J = 16 cps, 1 H), a crude quartet for the allyl methylene at δ 2.90 (J = 7 cps, 2 H), a sharp doublet for the phosphorus methyls at δ 2.09 (J = 13.5 cps, 6 H), and a triplet for the terminal methyl group at δ 1.30 (J = 7 cps, 3 H).

V, R = CH_3, R′ = C_6H_5, X = Br.—The ir spectrum ($CHCl_3$) displayed bands at 2450 (P-H), 1587 (C=C), 1570, 1447, and 1294 cm^{-1}. The nmr spectrum (TFA) showed an aromatic multiplet at δ 7.40–7.95 (5 H), the vinyl proton as two doublets at δ 7.13 and 6.83 (J = 6 cps, 17.5 cps apart, 1 H), and the phosphorus methyls as two doublets at δ 2.35 and 2.25 (J = 15 cps, 5 cps apart, 6 H).

Anal. Calcd for $C_{10}H_{13}Br_2P$: C, 37.07; H, 4.07; Br, 49.31; P, 9.55. Found: C, 37.50; H, 4.07; Br, 48.04; P, 9.91.

V, R = CH_2CH_3, R′ = CH_3, X = Br.—The ir spectrum ($CHCl_3$) showed bands at 2430 (P-H), 1615 (C=C), 1450, and 1370 cm^{-1}. The nmr spectrum (TFA) displayed the vinyl proton as a crude doublet at δ 6.52 (J = 13.5 cps, 1 H), the methylenes next to phosphorus as a multiplet at δ 2.35–3.00 (4 H), the allyl methyl group as a broadened singlet at δ 1.70 (3 H), and the methyls on the ethyl groups as a triplet at δ 1.32 (J = 7.5 cps, 6 H).

V, R = CH_2CH_3, R′ = C_6H_5, X = Br.—The ir spectrum (KBr) exhibited bands at 2260 (P-H), 1592, 1572, 1490 (C=C), 1448, and 1406 cm^{-1}. The nmr spectrum (TFA) showed an aromatic multiplet at δ 7.35–7.95 (5 H), the vinyl proton as a doublet at δ 7.08 (J = 7.5 cps, 1 H), the methylenes next to phosphorus as a multiplet at δ 2.3–3.1 (4 H), and the methyl groups as two triplets at δ 1.70 and 1.34 (J = 7 cps each, 6 H).

Anal. Calcd for $C_{12}H_{17}Br_2P$: C, 40.94; H, 4.87; Br, 45.40; P, 8.80. Found: C, 40.86; H, 4.92; Br, 45.12; P, 9.13.

V, R = $C_6H_5CH_2$, R′ = CH_3, X = Cl.—The nmr spectrum exhibited an aromatic singlet at δ 3.43 (10 H), the vinyl proton as two crude doublets at δ 5.89 and 6.15 (J = 7 cps each, 16 cps apart, 1 H), the benzyl protons as two crude doublets at δ 3.80 and 4.05 (J = 5 cps each, 15 cps apart, 4 H), and the methyl protons as a close doublet at δ 2.42 ($J \approx 0.5$ cps, 3 H).

VI, R = C_2H_5, R′ = C_6H_5, X = Br.—To a dry 50-ml tetrahydrofuran suspension of 3.0 g of diethyl-1-(2-bromo-2-phenylethenyl)phosphine hydrobromide was added 1.0 ml of pyridine. The mixture was stirred under nitrogen at 30–40° for 5 hr. The mixture was filtered and the filtrate stripped, leaving a gummy yellow material. The residue was recrystallized from ether–acetonitrile–methanol: yield, 1.2 g of light yellow powder (52%); mp *ca.* 27°. The ir spectrum ($CHCl_3$) showed bands at 1670, 1585, 1572, 1487, and 1448 cm^{-1} and no PH band at 2260 cm^{-1}. The nmr spectrum ($CDCl_3$) displayed an aromatic mul-

tiplet at δ 7.2–7.8 (5 H), a broad vinyl singlet at δ 6.88 (1 H), and two merged multiplets for the ethyl groups at δ 1.6–2.3 and 0.8–1.6 (10 H).

Diphenyl-1-butynylphosphine.—Approximately 20 ml of 1-butyne (Matheson) was condensed through an 8-mm glass U-tube in a Dry Ice bath into a 3-neck flask in a Dry Ice bath and under a nitrogen atmosphere. To the condensate was added 100 ml of dry tetrahydrofuran followed by 125 ml of 1.6 *M* *n*-butyllithium in hexane (Foote) over a 30-min period. The mixture was stirred for 20 min and warmed to ice bath temperature. An 80-ml dry tetrahydrofuran solution of 44.00 g of diphenylphosphinous chloride (Aldrich) was added during a 30-min period with stirring. The mixture was stirred at room temperature for 20 min and the solvent stripped. Ether (500 ml) was added to the residue, the mixture was filtered, and the ether was stripped from the filtrate. The resultant dark liquid was distilled through a 10-cm Vigeraux column at 0.45 mm, collecting one fraction (small amount of forerun discarded), bp 133–136°, to give 41.80 g of colorless liquid (87.9%). The ir spectrum ($CHCl_3$) showed significant absorptions at 2186 (C≡C, strong), 1478, 1437 (phenyl-P), and 1312 cm^{-1}. The nmr spectrum ($CDCl_3$) exhibited an aromatic multiplet at δ 7.1–7.7 (10 H), the allyl protons as a quartet (J = 7.5 cps) at δ 2.37 showing fine splitting ($J \approx 1.5$ cps, 2 H), and the terminal methyl group at δ 1.15 as a triplet (J = 7.5 cps, 3 H).

Diphenyl-1-(2-bromobutenyl)phosphine.—Into a solution of 1.15 g of diphenyl-1-butynylphosphine dissolved in 50 ml of benzene, hydrogen bromide was bubbled with stirring for 10 min and the solvent stripped to leave 1.54 g of red-yellow oil (quant). The ir spectrum ($CHCl_3$) showed bands at 1590 (C=C), 1485, and 1440 cm^{-1}. The nmr spectrum ($CDCl_3$) showed an aromatic multiplet at δ 7.20–7.60 with a sharp peak at δ 7.34 (10 H), a vinyl triplet at δ 6.53 (J = 1 cps, 1 H), the allyl methylene as a quartet at δ 2.67 (J = 7 cps) with fine splitting ($J \approx 1$ cps, 2 H), and the terminal methyl groups as a triplet at δ 1.20 (J = 7 cps, 3 H).

The bromophosphine was dissolved in 10 ml of acetone, and 3% hydrogen peroxide (aqueous) was added with stirring until the mixture was barely translucent. Acetone was added (a few drops) until the mixture was clear, and the solvent was allowed to evaporate to dryness in air. Water was added and the mixture filtered to leave 1.64 g of white solid (99% from the alkynylphosphine). Recrystallization from ethanol–water provided the analytical sample, mp 118–120°. The ir spectrum ($CHCl_3$) displayed the phosphoryl group at 1180 cm^{-1}. The nmr spectrum exhibited an aromatic multiplet at δ 7.00–7.55 (10 H), a vinyl doublet at δ 6.44 (J = 15.5 cps) with each peak split to a fine triplet (J = 1 cps, 1 H), the allyl methylene as a quartet at δ 2.60 (J = 7 cps) showing a small coupling constant ($J \approx 1$ cps, 2 H), and the terminal methyl as a triplet at δ 1.14 (J = 7 cps, 3 H).

Anal. Calcd for $C_{16}H_{16}BrOP$: C, 57.33; H, 4.81; Br, 23.84; P, 9.24. Found: C, 57.20; H, 4.76; Br, 23.92; P, 9.42.

Registry No.—IVa, 20439-89-8; IVb, 20439-90-1; IVa, b (picrate), 20439-91-2; IVc, 20439-92-3; IVd, 20439-93-4; IVc/d (picrate), 20439-94-5; IVe, 20439-95-6; IVf, 20439-96-7; IVe, f (picrate), 20439-97-8; IVg, 20439-98-9; IVh, 20439-99-0; IVg, h (picrate), 20440-00-0; IVi, 20440-01-1; IVi (picrate), 20440-02-2; IVj, 20440-03-3; IVj (picrate), 20440-04-4; IVk, 20440-05-5; IVk (picrate), 20440-06-6; IVl, 20440-07-7; IVl (picrate), 20440-08-8; Va, 20440-09-9; Vc, 20440-10-2; Vf, 20440-11-3; Vg, 20446-21-3; Vl, 20446-22-4; VIg, 20446-23-5; diphenyl-1-butynylphosphine, 20446-24-6; diphenyl-1-(2-bromobutenyl)phosphine, 20446-25-7; phosphoryl derivative of diphenyl-1-(2-bromobutenyl)phosphine, 20446-20-2.

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A Convenient, Synthetic Pathway to Dialkyl-1-alkynylphosphines

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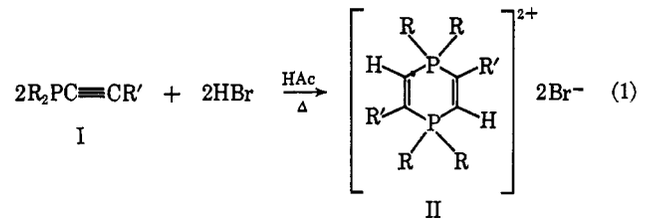
A new, convenient preparation of dialkyl-1-alkynylphosphines employing the readily available diethyl phosphorochloridite is described.

Interest in the preparation of dialkyl-1-alkynylphosphines (I, R = alkyl) was aroused by the discovery in this laboratory that the P-phenylated analogs are precursors to the P,P′-tetraphenylated 1,4-diphosphoniacyclohexadiene-2,5 salts (II) (eq 1).[3,4]



$$2R_2PC{\equiv}CR' + 2HBr \xrightarrow[\Delta]{HAc} [\text{II}]^{2+}\,2Br^- \quad (1)$$

I

R = C_6H_5
R′ = H, C_6H_5

A recent review on alkynylphosphines reveals the shortage of useful synthetic approaches to the dialkyl-1-alkynylphosphines.[5] Reaction of an alkynyllithium with the proper dialkylphosphinous halide (III) constitutes the most direct method of preparation of these compounds (eq 2).[6] This method depends upon the availability of the dialkylphosphinous chlorides.

$$\underset{\text{III}}{R_2PCl} + LiC{\equiv}CR' \longrightarrow \underset{\text{I}}{R_2PC{\equiv}CR'} + LiCl \quad (2)$$

Dialkylation of phosphorus trichloride is not readily achieved by alkyl Grignards unless the alkyl group is sterically demanding.[7] An example of the latter is the preparation of diisopropylphosphinous chloride from the reaction of isopropyl magnesium bromide with phosphorus trichloride (eq 3).[8]

$$2(CH_3)_2CHMgBr + PCl_3 \longrightarrow [(CH_3)_2CH]_2PCl + MgBr_2 + MgCl_2 \quad (3)$$

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