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 ($C \equiv C$, 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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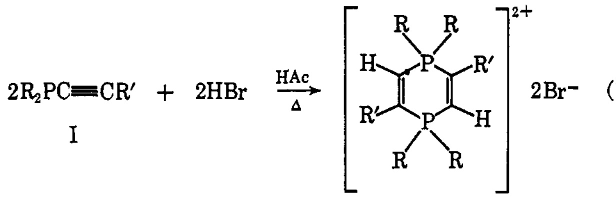
A new, convenient preparation of dialkyl-1-alkynylphosphines employing the readily available diethyl phosphorochloridite is described.

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]



(1)

I

II

$R = C_6H_5$
$R' = H, C_6H_5$

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.

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

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]

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

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[1] NASA Predoctoral Fellow, 1966–1969; NDEA Predoctoral Fellow, 1967–1968; NSF Predoctoral Fellow, 1969–1970.

[2] NDEA Predoctoral Fellow, 1965–1969.

[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] W. Voskuil and J. F. Arens, *Rec. Trav. Chim. Pays Bas*, **81**, 993 (1962).

[7] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950, p 16.

[8] W. Voskuil and J. F. Arens, *Rec. Trav. Chim. Pays Bas*, **82**, 302 (1963).

In our early attempts at obtaining dimethyl and diethylphosphinous chlorides, we employed many of the known methods of preparation of these compounds and found them to be badly lacking.[9,10] Two of these routes are summarized below (Schemes I and II).

SCHEME I

$$PCl_3 + 2HNR_2' \longrightarrow Cl_2PNR_2' + [R_2'NH_2]Cl$$

$$R_2'NPCl_2 + 2RMgX \longrightarrow R_2PNR_2' + MgX_2 + MgCl_2$$

$$R_2PNR_2' + 2HCl \longrightarrow \underset{\text{III}}{R_2PCl} + [R_2'NH_2]Cl$$

SCHEME II

$$\underset{\text{(excess)}}{RMgX} + PSCl_3 \longrightarrow [R_2P(S)]_2 + ?$$

$$[R_2P(S)]_2 + C_6H_5PCl_2 \longrightarrow \underset{\text{III}}{2R_2PCl} + ?$$

Not only are these compounds obtained in low yields by the methods shown above, but they are also pyrophoric and, consequently, difficult to handle.

We wish to report here a new, versatile, convenient approach to the P-dimethyl-, diethyl-, and dibenzylalkynylphosphines.

Reaction of the commercially available diethyl phosphorochloridite (IV) with an alkynyllithium can be easily controlled to yield the diethyl alkynyl-1-phosphonite (V) (eq 4). Reaction of the unisolated phosphonite V with 2 mol of methyl, ethyl, or benzyl magnesium halide yields the corresponding P-dialkyl-1-alkynylphosphine with little difficulty (eq 5).

$$\underset{\text{IV}}{(CH_3CH_2O)_2PCl} + LiC\equiv CR' \longrightarrow \underset{\text{V}}{(CH_3CH_2O)_2PC\equiv CR'} + LiCl \tag{4}$$

$$\underset{\text{V}}{(CH_3CH_2O)_2PC\equiv CR'} + 2RMgX \longrightarrow \underset{\text{I}}{R_2PC\equiv CR'} + (CH_3CH_2O)_2Mg + MgX_2 \tag{5}$$

$$R' = H,\ CH_3,\ C_2H_5,\ C_6H_5$$

$$R = CH_3,\ CH_3CH_2,\ CH_2C_6H_5$$

Some of the phosphines produced in this manner are listed in Table I along with their boiling points and yields.

It is relatively simple to prepare the starting diethyl phosphorochloridite by the known disproportionation reaction of phosphorus trichloride and triethyl phosphite (eq 6).[11]

$$PCl_3 + (CH_3CH_2O)_3P \rightleftharpoons \underset{\text{VI}}{(CH_3CH_2O)PCl_2} + \underset{\text{IV}}{(CH_3CH_2O)_2PCl} \tag{6}$$

Either the diethyl phosphorochloridite (IV) or ethyl phosphorodichloridite (VI) can be obtained in very pure form by employing adequate distillation procedures.

The success of this method for preparing dialkyl-1-alkynylphosphines is easily explained by the reasonable assumption that the chloride ion is much more easily displaced than the ethoxide ion. It is also probable that the great difference in rates of displacement of these two groups may involve the nature of the cation or the hydrocarbon moiety of the organometallic reagent. Diethyl ethynylphosphonite was prepared from the monomagnesium bromide salt of acetylene, indicating that the metal is not critical.

In this connection, it is interesting to note that the reaction of 1 mol of alkynyllithium with phosphorus trichloride, followed by addition of 2 mol of alkyl Grignard, does lead to a higher yield of the dialkyl-1-alkynylphosphine than if the Grignard is added first (eq 7 and 8).

$$PCl_3 + LiC\equiv CR' \longrightarrow Cl_2PC\equiv CR' + LiCl \tag{7}$$

$$R'C\equiv CPCl_2 + 2RMgX \longrightarrow R_2PC\equiv CR' + MgX_2 + MgCl_2 \tag{8}$$

The P-methyl, ethyl, and benzyl derivatives, however, can be obtained by this path only with some degree of hazard and in low yields. Trisalkynylphosphines are probably obtained as by-products, for, in one instance, detonation occurred upon attempted distillation of the crude mixture.

The dialkyl-1-alkynylphosphines prepared in this work were very air-sensitive, and they were converted to the corresponding 1,4-diphosphoniacyclohexadiene-2,5 salts immediately after preparation and characterization by nuclear magnetic resonance and infrared spectroscopy. Formation of these salts is discussed in another paper.

Experimental Section

All of the reactions were run under nitrogen, from the introduction of diethyl phosphorochloridite until after the addition of water. Lithium phenylacetylide was prepared by slowly adding 0.10 mol of *n*-butyllithium in hexane (63 ml of 1.6 *M* solution, Foote Chemical Co.) to a tetrahydrofuran solution of phenylacetylene immersed in an ice bath. Butynyllithium was prepared by condensing *ca.* 15 ml of 1-butyne in a Dry Ice bath, diluting with tetrahydrofuran, and slowly adding 0.10 mol of *n*-butyllithium. Propynyllithium was prepared in the same manner as butynyllithium, or the commercially available material (Foote) was used. This material existed primarily as a suspension when added to tetrahydrofuran. Tetrahydrofuran was dried over calcium hydride for 3–4 days and distilled from calcium hydride. The Grignard reagents were prepared in the usual manner in dry ether. Boiling points are uncorrected.

Preparation of Dialkyl-1-alkynylphosphines. General Procedure.—Diethyl phosphorochloridite (15.6 g, 0.10 mol) dissolved in 50–150 ml of tetrahydrofuran was immersed in a Dry Ice bath. A 50–100-ml suspension of 0.10 mol of the alkynyllithium compound in tetrahydrofuran was added with stirring over a 30–50-min period. The mixture was allowed to warm to room temperature, stirred for 30 min, and cooled in an ice bath. A quantity of 0.2 mol of the corresponding Grignard reagent in 100–150 ml of ether was added with stirring over a 30–90-min period. The mixture was stirred for 2–4 hr at room temperature and cooled in an ice bath, and 100 ml of saturated ammonium chloride solution was slowly added. Water (300 ml) was added, followed by 200 ml of ether. The phases were separated, and the ether was washed twice with water, dried ($MgSO_4$ or Na_2SO_4), and evaporated. The residue was distilled (short head or 10-cm Vigreux) at reduced pressure to yield the phosphine as a colorless liquid.

Spectra are as follows.

Dimethyl-1-butylnylphosphine.—The ir spectrum ($CHCl_3$) showed bands at 4.58 ($C\equiv C$), 7.00, 7.60, 10.55, and 10.98 μ. The nmr spectrum ($CDCl_3$) displayed a crude quartet at δ 2.32 (J = 7.5 cps, 2 H), and a doublet at δ 1.27 for the methyl groups on phosphorus (J = 3.5 cps) above the terminal methyl triplet at δ 1.17 (J = 7.5 cps, 9 H together).

Dimethyl(phenylethynyl)phosphine.—The ir spectrum ($CHCl_3$) showed absorptions at 4.65 ($C\equiv C$), 6.26, 6.72, 7.00, 10.57, and 11.05 μ. The nmr spectrum ($CDCl_3$) exhibited a complex aromatic multiplet at δ 7.10–7.55 (5 H) and a methyl doublet at δ 1.33 (J = 4 cps, 6 H).

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(10) G. W. Parshall, *J. Inorg. Nucl. Chem.*, **12**, 372 (1960).

(11) H. G. Cook and G. More, *J. Chem. Soc.*, 2921 (1949).

TABLE I

Compd	Registry no.	Bp, °C (mm)	Yield, % (after distillation)
$(CH_3)_2PC\equiv CC_2H_5$	20505–07–1	76–80 (90)	20[b]
$(CH_3)_2PC\equiv CC_6H_5$	30505–08–2	62–65 (0.6)	57
$(C_2H_5)_2PC\equiv CCH_3$[a]	6224–89–1	84–85 (50)	50
$(C_2H_5)_2PC\equiv CC_6H_5$[a]	7528–15–6	105–107 (0.7)	47
$(C_6H_5CH_2)_2PC\equiv CCH_3$	20505–11–7	168–171 (0.6)	16[c]
$(C_2H_5O)_2PC\equiv CH$	20505–16–2	75–80 (20)	30[d]

[a] C. Charrier, M. P. Simonnin, W. Chookiewicz, and P. Cadlot, *Compt. Rend.*, **258,** 1537 (1964). [b] Adequate precautions were not taken to account for the low volatility of the product, and the yield was probably higher. [c] This product oxidizes fairly rapidly, and exposure of the reaction mixture to air during work-up probably reduced the yield considerably. [d] Polymerization of this product occurs when heated, decreasing the yield.

Diethyl-1-propynylphosphine.—The ir spectrum ($CHCl_3$) showed absorptions at 4.57 ($C\equiv C$), 6.77, 8.10 (broad), and 9.71 μ. The nmr spectrum ($CDCl_3$) displayed the allyl methyl as a close doublet at δ 1.96 ($J = 1$ cps) above the edge of a complex multiplet representing the ethyl groups on phosphorus at δ 0.80–2.10.

Diethyl(phenylethynyl)phosphine.—The ir spectrum (film) displayed bands at 4.62 ($C\equiv C$), 6.26, 6.71, 6.88, and 11.97 μ. The nmr spectrum ($CDCl_3$) exhibited a complex aromatic region at δ 7.15–7.60 (5 H) and a complex aliphatic region at δ 0.85–2.00 (10 H) for the ethyl groups on phosphorus.

Dibenzyl-1-propynylphosphine.—The ir spectrum ($CHCl_3$) showed absorptions at 4.61 ($C\equiv C$), 6.29, 6.72, 6.90, and 7.09 μ. The nmr spectrum ($CDCl_3$) displayed an aromatic singlet at δ 7.30 (10 H), a doublet at δ 2.90 ($J = 2$ cps) for the benzyl protons (4 H), and a doublet at δ 1.80 ($J = 1$ cps) for the allyl methyl (3 H).

Diethyl Ethynylphosphonite.—The ir spectrum (film) showed bands at 3.08 ($\equiv CH$), 4.91 ($C\equiv C$), 7.22, 9.72 (broad, P—O), and 10.80 μ (broad, P—O). The nmr spectrum ($CDCl_3$) exhibited a multiplet at δ 3.6–4.3 for the methylenes in the ethyl groups (4 H), a doublet at δ 3.09 ($J = 2$ cps) for the acetylenic proton (1 H), and a crude triplet at δ 1.29 ($J = 7$ cps) for the methyl groups (6 H).

Diisopropyl-1-alkynylphosphines.—Diisopropylphosphinous chloride was prepared from two equivalents of isopropyl Grignard reagent and one equivalent of phosphorus trichloride as described by W. Voskuil.[8] The diisopropyl-1-alkynylphosphines were prepared by adding diisopropylphosphinous chloride to a dry tetrahydrofuran solution (or suspension) of the prepared alkynyllithium (or Grignard) compound in a Dry Ice bath, and was worked up in the same manner as before. Boiling points and spectra of phosphines prepared are as follows.

Diisopropylethynylphosphine had bp 43–45° (11 mm), 31% yield. The ir spectrum (film) displayed absorptions at 3.04 ($\equiv CH$), 4.88 ($C\equiv C$), 6.83, 7.20, and 7.30 μ. The nmr spectrum ($CDCl_3$) exhibited a doublet at δ 2.86 ($J = 9.5$ cps, 1 H) for the acetylenic proton, a broad multiplet at δ 1.54–2.38 (2 H) for the methynyl protons next to phosphorus, and a nine-line pattern at δ 0.90–1.54 (12 H) which seems to include three triplets ($J = 7$ cps) at δ 1.02, 1.19, and 1.24 (9.5 cps apart).

Diisopropyl-1-pentynylphosphine had bp 68–69° (1.25 mm), 26.1% yield. The ir spectrum ($CHCl_3$) showed bands at 4.60 ($C\equiv C$), 6.85, 7.21, and 7.30 μ. The nmr spectrum ($CDCl_3$) displayed two *merged* multiplets, one as a basic triplet at δ 2.32 ($J = 6$–7 cps), and the other as a complex pattern at δ 0.8–2.2 with the more intense peaks in the upfield half.

Diisopropyl-1-octynylphosphine had bp 89–93° (0.4 mm), 48.3% yield. The ir spectrum ($CHCl_3$) showed absorptions at 4.58 ($C\equiv C$), 6.82, 7.21, and 7.30 μ. The nmr spectrum ($CDCl_3$) displayed two *merged* multiplets, one at δ 2.1–2.5 appearing as a crude triplet at δ 2.30 ($J \approx 6$ cps), and the other as a complex pattern at δ 0.6–2.1 with the more intense peaks in the region δ 0.6–1.6.

Diisopropyl(phenylethynyl)phosphine had bp 116–120° (0.75 mm), 36% yield. The ir spectrum (film) displayed bands at 4.60 ($C\equiv C$), 6.24, 6.70, 6.82, 7.20, and 7.30 μ. The nmr spectrum ($CDCl_3$) exhibited an aromatic multiplet at δ 7.1–7.6 (5 H), a broad multiplet at δ 1.53–2.25 (2 H) for the methynyl protons next to phosphorus, and an eight-line pattern at δ 0.93–1.48 (12 H) for the methyl protons, which appears to be four doublets at δ 1.33, 1.28, 1.14, and 1.01, each having a coupling constant of 6–6.5 cps and each having a more intense downfield peak.

Registry No.—Diisopropylethynylphosphine, 20505-12-8; diisopropyl-1-pentynyl phosphine 20505-13-9; diisopropyl-1-octynylphosphine, 20505-14-0; diisopropyl(phenylethynyl)phosphine, 20505-15-1.

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