A New Organophosphorus Heterocycle

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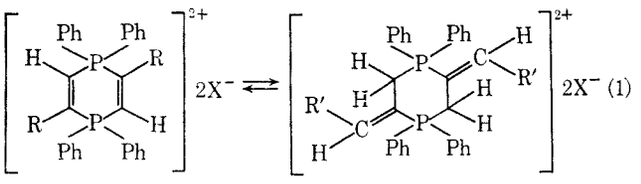
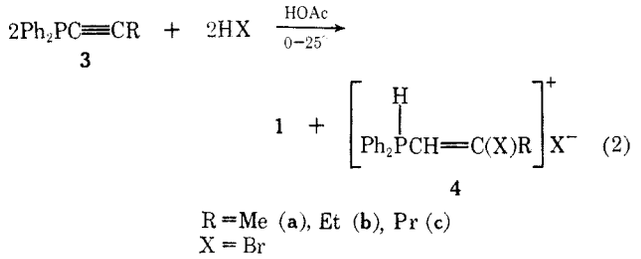
A new organophosphorus heterocyclic system, the 2,5-alkylidene-1,4-diphosphoniacyclohexane dihalide salts (**2**), was obtained by the tautomerization of the endocyclic diene isomers **1** in boiling glacial acetic acid, by the treatment of diphenyl-1-(alkylalkynyl)phosphine (**3**) with HX in glacial acetic acid, and by the cyclization of β-halovinylphosphine hydrohalides (**4**) obtained in the formation of **2**. The relative stability of systems **1** and **2** and the mechanism of formation of these rings are discussed. Basic hydrolysis of system **2** leads, unexpectedly, to a monophosphine oxide. The mechanism of hydrolysis is also discussed. Proton nmr spectra (60 MHz) of the various examples of **1**, **2**, and **3** are also included. The 100-MHz nmr spectrum of one example of system **2** is reproduced in the paper.

Only two examples of the endocyclic diene system 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexadiene-2,5 dihalides (**1**) have been reported.[1,2] Neither of these compounds (R = H, C_6H_5; X = Br, Cl) is capable of undergoing tautomerization to the exocyclic diene isomer **2** (eq 1).



1 **2**

Examples of **1** in which the substituents at the 2 and 5 positions are such that tautomerization to the previously unreported exocyclic diene system **2** is possible were prepared by reacting the proper diphenyl-1-alkynylphosphines **3** with hydrogen bromide in glacial acetic acid at 0–25° (eq 2).

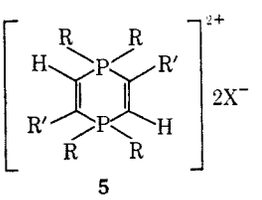


R = Me (**a**), Et (**b**), Pr (**c**)
X = Br

It was possible to isolate diphenyl-1-(2-bromo-2-alkylethenyl)phosphine hydrobromides (**4**) in some cases. These data are summarized in Table I.

It was found that refluxing glacial acetic acid caused complete conversion of the endocyclic dienes **1a** (R = Me), **b** (R = Et), and **c** (R = Pr) into the corresponding exocyclic diene tautomers **2a** (R′ = H), **b** (R′ = Me), and **c** (R = Pr), respectively (eq 1). The direct synthesis of these examples of the new organophosphorus heterocycle **2** from the corresponding diphenyl-1-alkynylphosphines **3a** (R = Me), **b** (R = Et), and **c** (R = Pr) was accomplished by using either hydrogen bromide in refluxing glacial acetic acid or hydrogen chloride in the same solvent at any temperature between 0 and 115°. Trifluoroacetic acid behaved in the same manner as hydrogen chloride while hydrogen iodide usually led to the isolation of only β-iodovinylphosphine hydriodides **4** (X = I).

Thermal isomerization of **1c** (R = Pr) into **2c** (R′ = Et) was complete after 0.5 hr at 150°. On the other hand, numerous attempts to convert various examples of **2** into the corresponding **1** isomer failed. It seems reasonable to conclude from these data that system **2** is more stable than system **1** even when R = Me and R′ = H (**1a** → **2a**). Increasing the steric demands of the substitutents at the 2 and 5 positions leads to an even greater difference in the relative stabilities of these two systems. While there was no difficulty in obtaining **2d**, R′ = pentyl, from diphenyl-1-octynylphosphine **3d**, it was not possible to prepare the endocyclic tautomeric **1d**, R = hexyl. The same was found to be true of diphenyl-1-(4-phenylbutynyl)phosphine (**3e**, R = CH_2CH_2Ph). Only the exocyclic isomer **2e** (R′ = CH_2Ph) could be obtained. Further support for the conclusion that steric hindrance between the phenyl groups on the phosphorus and the substituent at the 2 position plays a role in the isomerization of **1** to **2** is obtained from the stereochemistry at the double bonds of **2b**, **c**, **d**, and **e**. The substituent R′ is always found to be *trans* to the nearest phosphorus atom. This can be seen from the proton nmr spectra of these compounds. A reproduction of the spectrum of **2d** is shown in Figure 1. If the endocyclic dienes are planar while the exocyclic isomers **2** are in a chair conformation (as is the homomorph, cyclohexadione-1,4), the steric hindrance between the groups at the 2 and 5 positions and the phosphorus substituents would be relieved upon isomerization of **1** into **2**. A series of P-alkylated endocyclic dienes **5** have been prepared by a variation of the methods used here[3] and the *p*-ethylated analog of **1a** (**5a**, R = Et; R′ = Me; X = Br) has been found to be planar by X-ray diffraction.[4]



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These results indicate that the degree of stabilization conferred upon system **1** by π-electron interaction with the phosphorus atom is rather small in spite of the positive ^{31}P chemical shifts found for the two previously re-

(1) A. M. Aguiar, K. C. Hansen, and G. S. Reddy, *J. Amer. Chem. Soc.*, **89**, 3067 (1967).
(2) A. M. Aguiar and K. C. Hansen, *ibid.*, **89**, 4235 (1967).
(3) A. M. Aguiar, J. R. S. Irelan, G. W. Prejean, J. P. John, and C. J. Morrow, *J. Org. Chem.*, **34**, 2681 (1969).
(4) L. Trefonas and R. Majeste, *J. Heterocycl. Chem.*, **6**, 269 (1969).

TABLE I

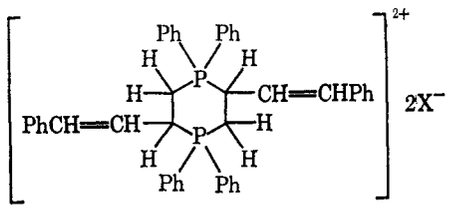
PRODUCTS OBTAINED IN THE TREATMENT OF DIPHENYL-1-ALKYNYLPHOSPHINES (3) WITH HX IN GLACIAL ACETIC ACID

				1			2			4			
3	R	Acid	Temp, °C	Yield, %	Mp, °C (dec)	Picrate mp, °C (dec)	Yield, %	Mp, °C (dec)	Picrate mp, °C (dec)	Yield, %	Mp, °C (dec)	Yield, %	Oxide mp, °C
a	Me	HBr	25	34	268–270	232–233	88[a]	272–276	218–220	48		79	132–135
			25	41			0			27	Orange liquid	93	118–120
	Et	HBr			331–333				245–247				
			115	0			96	320–322		0			
			25	0			85			0			
	Et	HCl						290–292					
			115	0			88			0			
b	Et												
			25	0			0			70	143–146		
	Et	HI			314–317[b]								
			115	0			70[c]	300–304		0			
	Et	TFA	25	0			96	300–302		0			
			25	22			0			0			
c	Pr	HBr			294–297	220–222		302–305	217–219				
			115	0			75			0			
			25	0			30			38		94	
d	Hex	HBr						262–264	225–227		Orange liquid		
			115	0			59			0			
e	CH_2CH_2Ph	HBr	25	0			74	268–270	206–208	0			
		HBr	25	17	268–271		0						
f									191–193[e]				
		HCl	115	0			66[d]	272–275		0			
			25	81			0			0			
g		HCl			218–220	215–217		214–217	82–84				
			115	0			41			0			

[a] From **1a** (X = Br) in hot acetic acid. [b] From **1b** (X = Br) with NaI in acetone–ethanol. [c] From **4b** (X = I) in hot acetic acid. [d] From **6f** (X = Cl) in hot acetic acid. [e] Picrate of **6f** or **2f**.

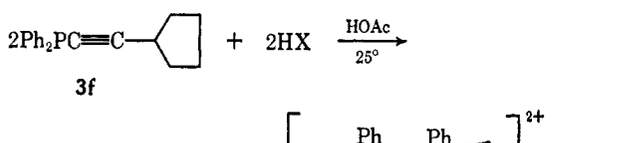
ported examples[1,2] of **1** (R = H, C_6H_5; X = Br, Cl).[5–7]

An interesting feature of the cyclization of **3e** (R = CH_2CH_2Ph) is the absence of any 1,4-diphosphoniacyclohexane having the double bond in conjugation with the side-chain phenyl group **8e**.

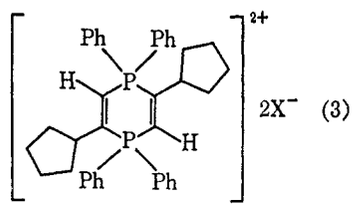


8e

It was felt that cyclization of diphenyl-1-(cycloalkylalkynyl)phosphines would be of interest. This is especially true of the cyclopentyl and cyclohexyl derivatives because of the possible difference in preference for endo- or exocyclic double bonds. Treatment of diphenyl-1-(cyclopentylethynyl)phosphine (**3f**) with hydrogen bromide in glacial acetic acid at room temperature gave the endocyclic diene **1f** (eq 3).



3f

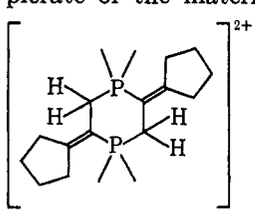


(3)

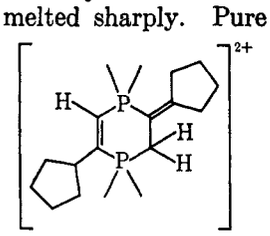
1f

X = Br, Cl

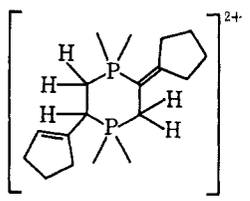
When **3f** was treated with hydrogen chloride at room temperature, a material was obtained which was either a 1:1 mixture of **1f** and the exocyclic diene isomer **2f** or, more likely, a monoendo-, monoexocyclic diene **6f** since the picrate of the material melted sharply. Pure **2f**



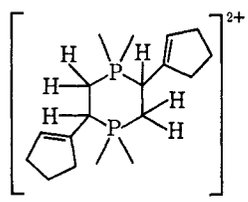
2f



6f



7f



8f

(5) Reduction of electrostatic repulsion between the positively charged phosphorus atoms in going from planar **1** to the chair conformation **2** no doubt plays a role in the greater stability of **2**. Herriot has approximated this difference to be 1.0 cal/mole: private communication from A. W. Herriot, Department of Chemistry, New York State University, Albany, N. Y.

(6) D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118 (1962).

(7) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *ibid.*, 2423 (1960).

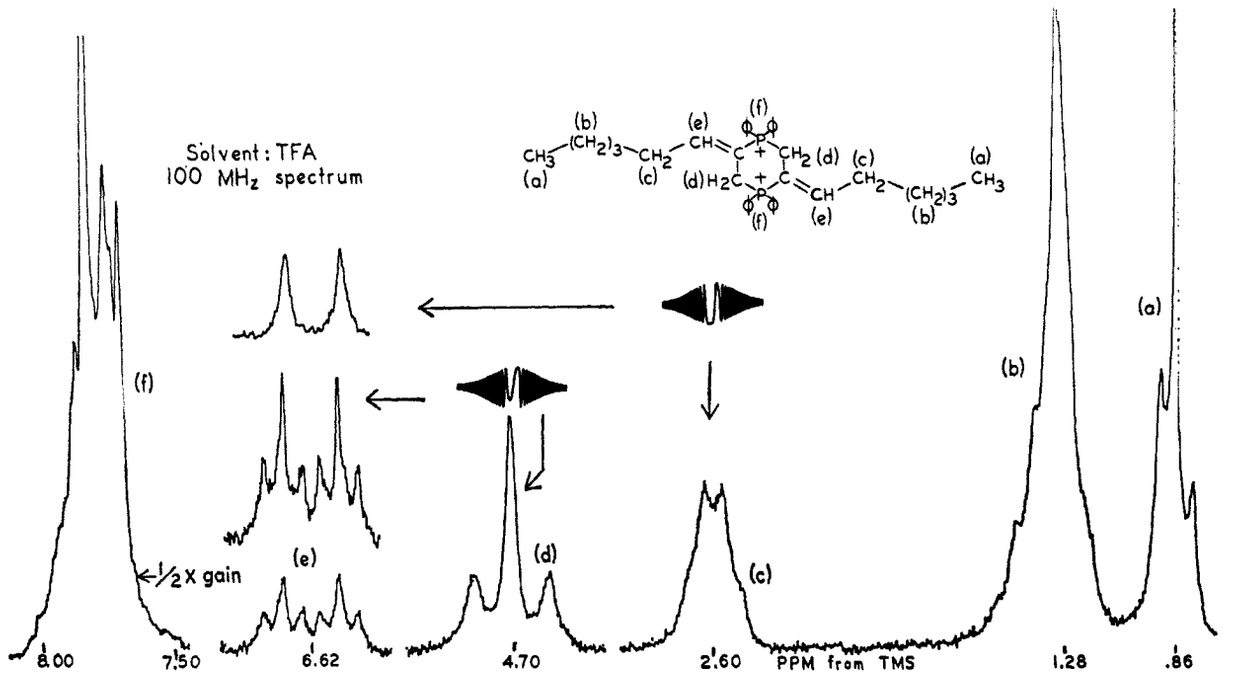
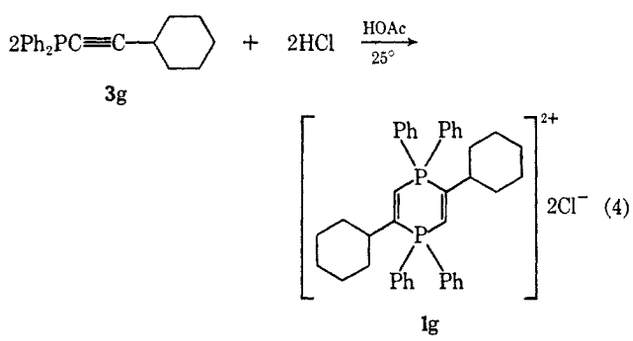


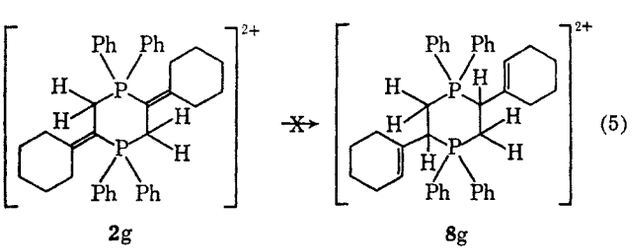
Figure 1.

was obtained either from **3f** by treatment with hydrogen chloride in refluxing glacial acetic acid or from **1f** by refluxing in glacial acetic acid. There was no evidence of the presence of tautomers having the double bond endocyclic to the cyclopentane ring such as **7f** or **8f**.

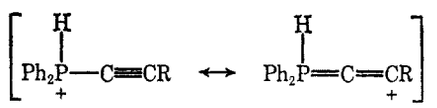
In contrast to the cyclopentylalkynylphosphine (**3f**), treatment of diphenyl(cyclohexylethynyl)phosphine (**3g**) with hydrogen chloride in glacial acetic acid at room temperature led to the pure endocyclic diene **1g** (eq 4).



The corresponding exocyclic diene isomer **2g** was obtained from **3g** with hydrogen chloride in refluxing glacial acetic acid. Although this compound has double bonds exocyclic to the cyclohexane ring, the bonds show no tendency to migrate *endo* to the cyclohexane rings to give **8g** (eq 5).

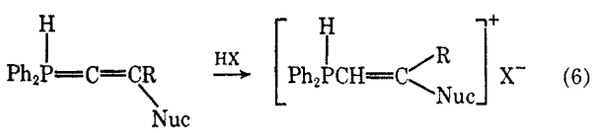


The possible pathways by which the cyclization of diphenyl-1-alkynylphosphines **3** into **1** and/or **2** occurs must begin with protonation of **3**. Protonation at the phosphorus atom must occur to some extent. Attack

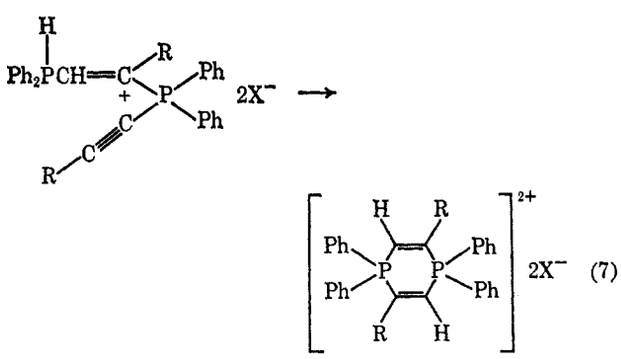


of a nucleophile (Nuc) at the β carbon is thus facilitated.

Further protonation of either of the two possible intermediates produced would lead to the same β-Nuc-vinylphosphine hydrohalide salt (eq 6).

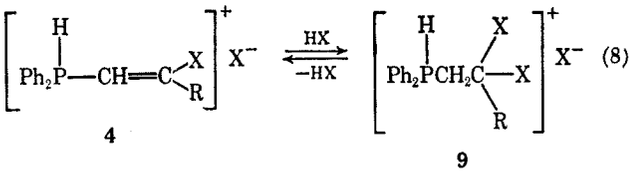


If the nucleophile is another molecule of phosphine, repetition of this acid-catalyzed Michael addition intramolecularly would lead to **1** (eq 7). When the nucleophile is the conjugate base of the acid used to catalyze the cyclization, *e.g.*, halide ion, then a β-halovinylphosphine hydrohalide **4** is produced. As was stated earlier, these have been isolated from the cyclizations involving hydrogen bromide at room temperature and are the only products isolated when hydrogen iodide is used. No



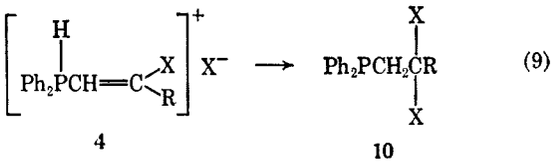
β-chloro or trifluoroacetyl vinylphosphine hydrochlorides or trifluoroacetates were isolated in this work. These data are in accord with expectations from such a mechanism. Iodide ion is known to be a better nucleophile than bromide; chloride and trifluoroacetate ions are very poor nucleophiles. Apparently iodide ion and, to a lesser extent, bromide ion compete effectively with the alkynyl-1-phosphines in addition to the β carbon.

It is possible that another mole of hydrogen halide adds to **4** to give a β,β-dihaloethylphosphine hydrohalide **9** (eq 8).



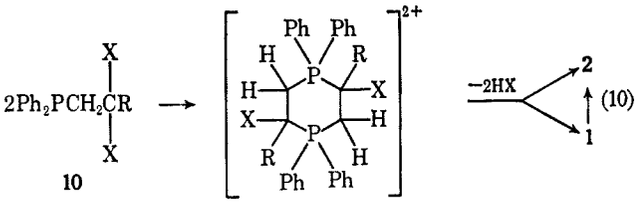
4 **9** (8)

Protolytic shift within **4** can lead to β,β-dihaloethylphosphines **10** (eq 9).

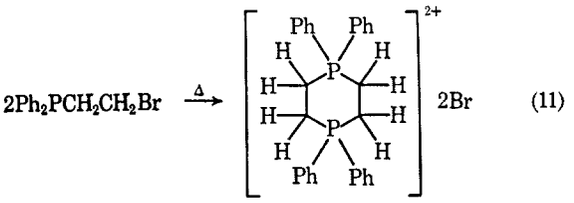


4 **10** (9)

Head-to-tail reaction of **10** would lead to cyclization

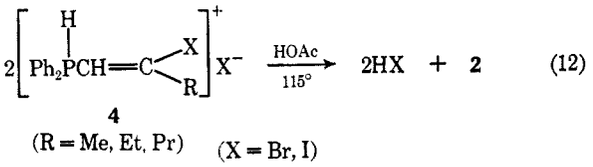


in analogy with the known cyclization of β-haloethylphosphines (eq 11).[8]



(11)

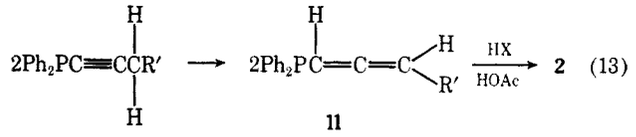
It has now been shown that diphenyl-1-(2-halo-2-alkylethenyl)phosphine hydrohalides (X = Br, I) are cyclized into **2** in refluxing glacial acetic acid (eq 12).



4

(R = Me, Et, Pr) (X = Br, I) (12)

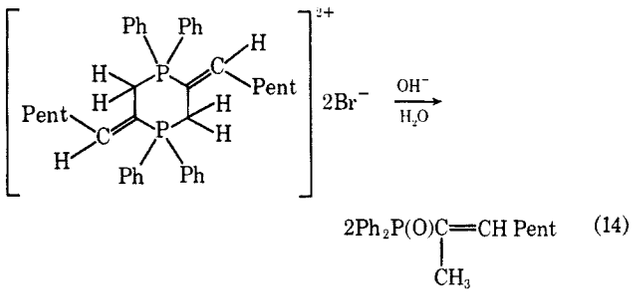
In the formation of **2** at room temperature from **3** employing hydrogen chloride or trifluoroacetic acid, **1** need not be an intermediate. This was shown by subjecting **1b** (R = Et, X = Br) to trifluoroacetic acid at room temperature in glacial acetic acid for 12 hr and isolating **1b** unchanged. This was an expected result since the proton nmr spectra of all of the examples of **1** as well as of **2** were taken of trifluoroacetic acid solutions of these compounds. Formation of **2** from **3** without the intermediacy of **1** may occur *via* the path shown in eq 10 or by tautomerization of **3** into the allenylphosphine **11** prior to cyclization (eq 13).



3 **11** (13)

It is known that *t*-phosphines will add to conjugated alkynes under acid-catalyzed conditions.[9] Further studies of allenyl-1-phosphines are now in progress.

Alkaline hydrolysis of this new organophosphorus heterocycle leads to monophosphine oxides (eq 14) rather than diphosphine monooxides as in the case of the saturated or monounsaturated 1,4-diphosphonium salts[10,11] (eq 15).



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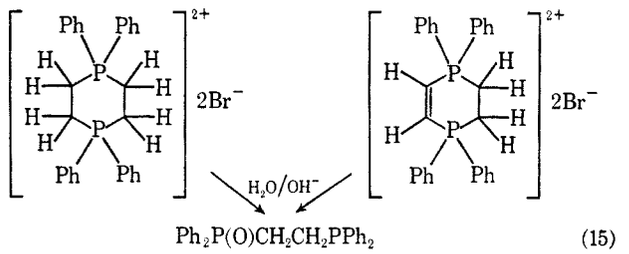
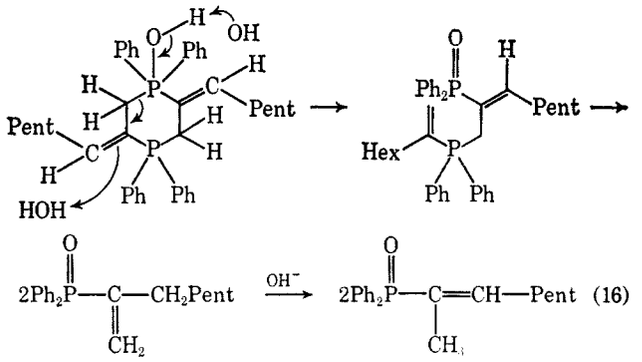


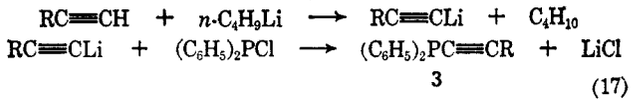
(15)

Presumably the initially formed hydroxyphosphorane decomposes *via* an allylic shift (eq 16).



(16)

All of the diphenyl-1-alkynylphosphines were prepared by converting the commercially available terminal alkyne to its metallic salt and reacting this with diphenylphosphinous chloride (eq 17).



3 (17)

(8) C. H. S. Hitchcock and F. G. Mann, *J. Chem. Soc.*, 2081 (1958).

(9) (a) D. Allen and J. C. Tebby, *Tetrahedron Lett.*, 2361 (1965); (b) H. Hoffmann and H. J. Diehr, *Chem. Ber.*, **98**, 364 (1965); (c) G. S. Reddy and C. D. Weis, *J. Org. Chem.*, **28**, 1822 (1963).

(10) A. M. Aguiar and H. J. Aguiar, *J. Amer. Chem. Soc.*, **88**, 4090 (1966).

(11) A. M. Aguiar, H. J. Aguiar, and D. J. Daigle, *ibid.*, **87**, 671 (1965).

Table II summarizes the data on these preparations.

TABLE II

PREPARATION OF DIPHENYL-1-ALKYNYLPHOSPHINES

a	R	Yield, %	Bp, °C (mm)
a	Me	82	130–131 (0.3)[a]
b	Et	88	133–134 (0.45)
c	Pr	77	132–134 (0.40)
d	Hex	80	152–152.5 (0.16)
e	CH_2CH_2Ph	64	Dec
f		81	175–178 (0.25)
g		63	212–214 (0.75)

[a] Lit.[12] bp 143° (0.1 mm).

Experimental Section

Preparation of Diphenyl-1-alkynylphosphines (3).—An equimolar amount of 1.6 *N* *n*-butyllithium in hexane (Foote Chemical Co.) was added dropwise to a rapidly stirred 10% solution of 0.1–0.2 mol of the liquid terminal alkyne (Farchan Chemical Co.) in tetrahydrofuran (dried by storing over calcium hydride for 3–4 days and distilling from calcium hydride just before use) at 0° under a nitrogen atmosphere. After the addition was complete (about 30 min), an equimolar amount of diphenylphosphinous chloride in tetrahydrofuran was added dropwise, with stirring, at 0°. The mixture was allowed to warm to room temperature with stirring (0.5–1 hr) and the tetrahydrofuran was stripped off at aspirator pressure using a warm water bath. The residual oil was dissolved in ether or (less commonly) chloroform and washed three times with about 20-ml portions of water. After the organic layer was dried over anhydrous sodium sulfate it was filtered, the solvent was stripped, and the residual oil was vacuum distilled.

But-1-yne, being a gas at room temperature, was condensed in a Dry Ice bath, tetrahydrofuran added, and *n*-butyllithium added to the alkyne solution in a Dry Ice bath. Propynyllithium was prepared in the same manner or the commercially available material (Foote) was used.

Treatment of Diphenyl-1-alkynylphosphines with Hydrogen Halides.—Slow passage of the hydrogen halide gas through a glacial acetic acid solution of the diphenyl-1-alkynylphosphine for 0.5 to 2 hr was carried out either at reflux or at room temperature with the aid of an ice–water bath. This was followed by standing in a sealed container under nitrogen for a period of 1 day to 2 weeks. The acetic acid was stripped off at aspirator pressure with the aid of a hot water bath and placed under vacuum at 70–80° for 3–4 hr. Trituration of the glassy material thus obtained with ether (followed in some cases by acetone trituration) gave the crystalline cyclic diphosphonium salts (1 and 2). These were recrystallized from methanol–ethyl acetate. Evaporation of the ether filtrate led to isolation of the diphenyl-1-(2-bromo-2-alkylethenyl)phosphine hydrohalide salts (4). When the hydrohalide was hydrogen iodide, 4 precipitated out of the glacial acetic acid solution.

Trifluoroacetic acid was added dropwise to a glacial acetic acid solution of 3, the solution was allowed to stand 10 min, the solvent was removed as before, and the resulting ditrifluoroacetate of 1 was obtained by acetone trituration.

Picrates were formed by mixing a methanol solution of the phosphonium salt with a methanol solution of sodium picrate from which the yellow solids precipitated immediately. They were recrystallized from methanol.

Diiodides prepared by metathetical reaction were obtained by adding an ethanol solution of the phosphonium dibromide to an acetone solution of sodium iodide and the white solid diiodide precipitated immediately.

Diperbromides were obtained by adding a methanol solution of bromine to a methanol solution of the phosphonium salt and the orange solid diperbromide precipitated.

Treatment of the Diphenyl-1-(2-bromo-2-alkylethenyl)phosphine Hydrohalides (4) with Refluxing Glacial Acetic Acid. General Procedure.—A suspension of the diphenyl-1-(2-bromo-2-alkenyl)phosphine hydrohalide in glacial acetic acid was refluxed for 1 to 2 hr. As the hydrogen halide was liberated, the suspended material went into solution. Upon cooling to room temperature the exocyclic diene phosphonium salt precipitated.

Preparation of Diphenyl-1-(2-bromo-2-alkylethenyl)phosphine Oxide.—The diphenyl-1-(2-bromo-2-alkylethenyl)phosphine or its hydrohalide was dissolved in acetone and 3% aqueous hydrogen peroxide was added up to cloudiness. Enough acetone was added to clear the cloudiness and the solution allowed to evaporate slowly. White solid crystallized out and this was recrystallized from ethanol–water.

Spectroscopic data for compound 3a (R = CH_3) follow: ir ($CHCl_3$) 4.58 (C≡C), 6.77, 6.98 μ (phenyl P); nmr ($CDCl_3$) δ 7.50–7.90 and 7.15–7.50 (10, aromatic), 2.02 (d, 3, J_{PH} = 2 Hz, methyl).

Spectroscopic data for compound 3b (R = C_2H_5) follow: ir ($CHCl_3$) 4.58 (C≡C), 6.77, 6.98 (phenyl P), 7.61 μ; nmr ($CDCl_3$) δ 7.42–7.84 and 7.10–7.42 (10, aromatic), 2.37 (q, 2, J = 7 Hz, methylene), 1.16 (t, 3, J = 7 Hz, methyl).

Spectroscopic data for compound 3c (R = C_3H_7) follow: ir ($CHCl_3$) 4.58 (C≡C), 6.77, 6.98 μ (phenyl P); nmr ($CDCl_3$) δ 7.42–7.84 and 7.11–7.42 (10, aromatic), 2.37 (t, 2, J = 7 Hz, allyl), 1.59 (6, 2, J = 7 Hz, $CH_2CH_2CH_3$), 0.99 (t, 3, J = 7 Hz, methyl).

Spectroscopic data for compound 3d (R = C_6H_{13}) follow: ir ($CHCl_3$) 4.59 (C≡C), 6.77, 6.98 (phenyl P), 8.29 μ; nmr ($CDCl_3$) δ 7.41–7.80 and 7.11–7.41 (10, aromatic), 2.41 (t, 2, J = 7 Hz, allyl), 1.08–1.80 and 0.67–1.08 (11, other protons).

Anal. Calcd for $C_{20}H_{23}P$: C, 81.63; H, 7.82; P, 10.54. Found: C, 82.00; H, 8.11; P, 10.03.

Compound 3e (R = $CH_2CH_2C_6H_5$) was purified by distillation in a molecular still at 180–184° (0.60–0.75 mm): ir ($CHCl_3$) 4.58 (C≡C), 6.69, 6.77, 6.89, 6.98 μ (phenyl P); nmr ($CDCl_3$) δ 7.34–7.73 and 7.13–7.34 (15, aromatic), 2.65–2.89 (4, methylenes).

Anal. Calcd for $C_{22}H_{19}P$: C, 83.82; H, 6.03; P, 10.14. Found: C, 83.80; H, 5.81; P, 9.95.

Spectroscopic data for compound 3f (R = cyclopentyl) follow: ir ($CHCl_3$) 4.57 (C≡C), 6.75, 6.96 μ (phenyl P); nmr ($CDCl_3$) δ 7.46–7.86 and 7.17–7.46 (10, aromatic), 2.60–3.15 (1, allyl), 1.45–2.30 (8, cyclopentyl).

Anal. Calcd for $C_{19}H_{19}P$: C, 82.01; H, 6.83; P, 11.15. Found: C, 81.34; H, 6.80; P, 10.13.

Spectroscopic data for compound 3g (R = cyclohexyl) follow: ir ($CHCl_3$) 4.60 (C≡C), 6.77, 6.90, 6.98 μ (phenyl P); nmr ($CDCl_3$) δ 7.46–7.82 and 7.17–7.46 (10, aromatic), 2.40–2.88 (1, allyl), 1.15–2.15 (10, cyclohexyl).

Anal. Calcd for $C_{20}H_{21}P$: C, 82.18; H, 7.19; P, 10.62. Found: C, 81.56; H, 7.44; P, 10.87.

Spectroscopic data for compound 1a (R = CH_3; X = Br) follow: ir (KBr) 6.94 (phenyl P), 9.00 μ (P+); nmr [TFA (trifluoroacetic acid)] δ 8.40 (t, 2, J = 25 Hz, vinyl), 7.66–8.21 (20, aromatic), 2.38–2.81 (6, methyl).

Elementary analysis was made on compound 1a (R = CH_3; X = picrate).

Anal. Calcd for $C_{42}H_{32}N_6O_{14}P_2$: C, 55.65; H, 5.35; N, 9.26; P, 6.83. Found: C, 55.65; H, 3.61; N, 9.26; P, 6.66.

Compound 1a (R = CH_3; X = Br_3) was obtained in 80% yield, mp 275–278° dec.

Anal. Calcd for $C_{30}H_{28}Br_6P_2$: Br, 51.65. Found: Br, 53.22.

Spectroscopic data for compound 1b (R = C_2H_5; X = Br) follow: nmr (TFA) δ 8.37 (t, 2, J = 26 Hz, vinyl), 7.52–8.18 (20, aromatic), 2.57–3.11 (4, allyl), 1.40 (t, 6, J = 7 Hz, methyl).

Spectroscopic data for compound 1c (R = C_3H_7; X = Br) follow: nmr (TFA) δ 8.46 (t, 2, J = 27 Hz, vinyl), 7.67–8.30 (20, aromatic), 2.55–3.12 (4, allyl), 1.73 (q, 4, J = 7 Hz, $CH_2CH_2CH_3$), 0.93 (t, 6, J = 7 Hz, methyl).

Elementary analysis was made on compound 1c (R = C_3H_7; X = picrate).

Anal. Calcd for $C_{46}H_{40}N_6O_{14}P_2$: C, 57.40; H, 4.16; N, 8.73; P, 6.43. Found: C, 57.30; H, 4.30; N, 8.82; P, 5.40.

Spectroscopic data for compound 1f (R = cyclopentyl; X = Br) follow: nmr (TFA) δ 8.52 (t, 2, J = 27 Hz, vinyl), 7.66–8.21 (20, aromatic), 2.65–3.50 (2, allyl), 1.45–2.15 (16, cyclopentyl).

Spectroscopic data for compound 1g (R = cyclohexyl; X = Cl) follow: nmr (TFA) δ 8.31 (t, 2, J = 28 Hz, vinyl, 7.66–

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

8.21 (20, aromatic), 2.35–3.17 (2, allyl), 0.90–2.10 (20, cyclohexyl).

Elementary analysis was performed on compound **1g** (**R = cyclohexyl; X = picrate**).

Anal. Calcd for $C_{52}H_{48}N_6O_{14}P_2$: C, 59.88; H, 4.70; N, 8.06; P, 5.95. Found: C, 60.01; H, 4.52; N, 8.11; P, 6.00.

Spectroscopic data for compound 2a (R′ = H; X = Br) follow: nmr (TFA) δ 7.52–8.25 (20, aromatic), 6.32 and 7.17 (AB, 4, J_{AB} = 22 Hz, vinyl), 4.79 (t, 4, J = 14 Hz, PCH_2).

Elementary analysis was performed on **2a** (R′ = H; X = picrate).

Anal. Calcd for $C_{42}H_{32}N_6O_{14}P_2$: C, 55.65; H, 3.53; N, 9.26; P, 6.83. Found: C, 55.79; H, 3.68; N, 9.22; P, 6.71.

Spectroscopic data for compound 2b (R′ = CH_3; X = Br) follow: nmr (TFA) δ 7.63–8.15 (20, aromatic), 6.55–7.55 (2, vinyl), 4.74 (t, 4, J = 14 Hz, PCH_2), 2.35 (d, 6, J = 7 Hz, methyl).

Elementary analysis was performed on compound **2b** (R′ = CH_3; X = picrate).

Anal. Calcd for $C_{44}H_{36}N_6O_{14}P_2$: C, 56.60; H, 3.85; N, 9.00; P, 6.64. Found: C, 56.48; H, 4.06; N, 9.01; P, 7.19.

Spectroscopic data for 2b (R′ = CH_3, X = Cl) follow: nmr (TFA) δ 7.50–8.15 (20, aromatic), 6.50–7.33 (2, vinyl), 4.55 (t, 4, J = 15 Hz, PCH_2), 2.37 (d, 6, J = 7 Hz, methyl).

Spectroscopic data for 2b (R′ = CH_3; X = I) follow: nmr (TFA) δ 7.58–8.17 (20, aromatic), 6.55–7.38 (2, vinyl), 4.70 (t, 4, J = 15 Hz, PCH_2), 2.33 (d, 6, J = 7 Hz, methyl).

Spectroscopic data for 2b (R′ = CH_3; X = $OCOF_3$) follow: nmr (TFA) δ 7.45–8.15 (20, aromatic), 6.50–7.30 (2, vinyl), 4.39 (t, 4, J = 14 Hz, PCH_2), 2.27 (d, 6, J = 7 Hz, methyl).

Spectroscopic data for 2c (R′ = C_2H_5; X = Br) follow: nmr (TFA) δ 7.60–8.15 (20, aromatic), 6.72 (d of t, 2, J_{PH} = 21.6 Hz, J_{HH} = 7 Hz, vinyl), 4.72 (t, 4, J = 14 Hz, PCH_2), 2.37–3.00 (4, allyl), 1.11 (t, 6, J = 7 Hz, methyl).

Compound 2c (R′ = C_2H_5; X = I) had mp 272–275°; nmr (CD_3SOCD_3) δ 7.57–8.18 (20, aromatic), 6.85 (d of t, 2, J_{PH} = 19 Hz, J_{HH} = 7 Hz, vinyl), 5.10 (t, 4, J = 7 Hz, PCH_2), 2.20–2.65 (4, allyl), 0.90 (t, 6, J = 7 Hz, methyl).

Compound 2c (R′ = C_2H_5; X = Br_3) had mp 290–295°; nmr (TFA) δ 7.46–8.13 (20, aromatic), 6.70 (d of t, 2, J_{PH} = 20.4 Hz, J_{HH} = 7 Hz, vinyl), 4.70 (t, 4, J = 15 Hz, PCH_2), 2.35–3.05 (4, allyl), 1.11 (t, 6, J = 7 Hz, methyl).

Elementary analysis was performed on **2c** (R′ = C_2H_5; X = picrate).

Anal. Calcd for $C_{46}H_{40}N_6O_{14}P_2$: C, 57.40; H, 4.16; N, 8.73; P, 6.43. Found: C, 57.40; H, 4.24; N, 8.80; P, 6.65.

Spectroscopic data for 2d (R′ = C_5H_{11}; X = Br) follow: ir (KBr) 6.22 (C=C), 6.95 (phenyl P), 9.02 μ (P+); nmr (TFA) δ 7.48–8.10 (20, aromatic), 6.61 (d of t, 2, J_{PH} = 20 Hz, J_{HH} = 7 Hz, vinyl), 4.72 (t, 4, J = 14 Hz, PCH_2), 2.40–2.85 (4, allyl), 1.15–1.65 and 0.70–1.15 (22, butyl).

Elementary analysis was performed on **2d** (R′ = C_5H_{11}; X = picrate).

Anal. Calcd for $C_{52}H_{52}N_6O_{14}P_2$: C, 59.65; H, 4.97; N, 8.00; P, 5.90. Found: C, 59.46; H, 5.19; N, 7.92; P, 4.99.

Spectroscopic data for 2e (R′ = $CH_2C_6H_5$; X = Br) follow: ir (KBr) 6.22 (C=C), 6.95 (phenyl P), 9.02 μ (P+); nmr (TFA) δ 6.65–7.50 and 7.50–8.20 (32, aromatic and vinyl), 4.91 (t, 4, J = 15 Hz, PCH_2), 3.88–4.28 (4, allyl–benzyl).

Elementary analyses was performed on **2e** (R′ = $CH_2C_6H_5$; X = picrate).

Anal. Calcd for $C_{56}H_{44}N_6O_{14}P_2$: C, 60.90; H, 4.05; N, 7.73; P, 5.70. Found: C, 60.89; H, 4.01; N, 7.53; P, 5.54.

Spectroscopic data on 2f (R′ = cyclopentylidene; X = Cl) follow: nmr (TFA) δ 7.50–8.22 (20, aromatic), 4.68 (t, 4, J = 13 Hz, PCH_2), 2.58–3.07 (8, allyl), 1.55–2.20 (8, cyclopentyl).

1,1,4,4-Tetraphenyl-1,4-diphosphonia-2-cyclopentylidene-5-cyclopentylcyclohexene-5 Dichloride (6f).—This compound was prepared in 66% yield: mp 270–274°; nmr (TFA) δ 8.52 (t, 1, J = 23 Hz, vinyl), 7.58–8.28 (20, aromatic), 4.76 (t, 2, J = 14 Hz, PCH_2), 2.50–3.33 (5, allyl), 1.43–2.17 (12, cyclopentyl).

6f dipicrate had mp 191–193°.

Anal. Calcd for $C_{50}H_{44}N_6O_{14}P_2$: C, 59.17; H, 4.37; N, 8.28; P, 6.10. Found: C, 59.04; H, 4.37; N, 8.28; P, 6.11.

Spectroscopic data for 2g (R′ = cyclohexylidene; X = Cl) follow: ir (KBr) 6.22 (C=C), 6.96 (phenyl P), 9.02 μ (P+); nmr (TFA) δ 7.33–8.38 (20, aromatic), 4.82 (t, 4, J = 14 Hz, PCH_2), 0.83–2.05, 2.05–2.42, and 2.42–2.87 (20, cyclohexane).

Elementary analysis was performed on **2g** (R′ = cyclohexylidene; X = picrate).

Anal. Calcd for $C_{52}H_{48}N_6O_{14}P_2$: C, 59.88; H, 4.70; N, 8.06; P, 5.95. Found: C, 59.31; H, 4.63; N, 7.86; P, 7.43.

Spectroscopic data for 4a (R = CH_3; X = Br) phosphine follow: ir ($CHCl_3$) 6.21 (C=C), 6.76, 6.95 μ (phenyl P); nmr ($CDCl_3$) δ 7.08–7.62 (10, aromatic), 6.46 (q, 1, J = Hz, vinyl), 2.36–2.52 (AB, 3, J = 1 Hz, methyl).

Spectroscopic data for 4a (R = CH_3; X = Br oxide) follow: ir ($CHCl_3$) 6.98 (phenyl P), 8.55 (P=O), 8.95 μ (P+); nmr ($CDCl_3$) δ 7.30–7.68 and 7.68–8.03 (10, aromatic), 6.70 (d of q, 1, J_{PH} = 16 Hz, J_{HH} = 1 Hz, vinyl), 2.51–2.65 (AB, 3, J = 1 Hz, methyl).

Anal. Calcd for $C_{15}H_{14}BrOP$: C, 56.11; H, 4.36; Br, 24.89; P, 9.64. Found: C, 56.08; H, 4.52; Br, 25.18; P, 9.38.

Spectroscopic data for 4b (R = C_2H_5; X = Br) phosphine follow: ir ($CHCl_3$) 6.22 (C=C), 6.28, 6.76, 6.97 μ (phenyl P); nmr ($CDCl_3$) δ 7.18–7.60 (10, aromatic), 6.48 (t, 1, J = 1 Hz, vinyl), 2.65 (d of q, J_{vinyl} = 1 Hz, J_{CH_3} = 7 Hz, allyl), 1.19 (t, 3, J = 7 Hz, methyl).

Spectroscopic data for 4b (R = C_2H_5; X = Br) oxide follow: ir ($CHCl_3$) 6.20 (C=C), 6.97 (phenyl P), 8.54 (P=O), 8.94 μ (P+); nmr ($CDCl_3$) δ 7.02–7.40 and 7.40–7.66 (10, aromatic), 6.45 (d of t, 1, J_{PH} = 15.5 Hz, J_{HH} = 1 Hz, vinyl), 2.60 (d of t, 2, J_{vinyl} = 1 Hz, J_{CH_3} = 7 Hz, allyl), 1.14 (t, 3, J = 7 Hz, methyl).

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.

Spectroscopic data for 4b (R = C_2H_5; X = I) hydriodide follow: ir ($CHCl_3$) 4.16 (PH), 6.26 (C=C), 6.95 (phenyl P), 9.01 μ (P+); nmr ($CDCl_3$) δ 7.32–7.83 and 8.00–8.43 (11, aromatic and vinyl), 3.01 (q, 2, J = 7 Hz, allyl), 1.23 (t, 3, J = 7 Hz, methyl).

Anal. Calcd for $C_{16}H_{17}I_2P$: I, 54.25. Found: I, 55.00.

Spectroscopic data for 4d (R = C_6H_{13}; X = Br) phosphine follow: ir ($CHCl_3$) 6.22 (C=C), 6.75, 6.95 μ (phenyl P); nmr ($CDCl_3$) δ 7.15–7.60 (10, aromatic), 6.51 (t, 1, J = 1 Hz, vinyl), 2.63 (d of t, 2, J_{vinyl} = 1 Hz, J_{CH_2} = 7 Hz, allyl), 0.70–1.10 and 1.10–1.95 (13, remainder of side chain).

Spectroscopic data for 4d (R = C_6H_{13}; X = Br) oxide follow: ir ($CHCl_3$) 6.20 (C=C), 6.96 (phenyl P), 8.51 μ (P=O); nmr ($CDCl_3$) δ 7.27–7.62, and 7.62–7.98 (10, aromatic), 6.66 (d of t, 1, J_{PH} = 17 Hz, J_{HH} = 1 Hz, vinyl), 2.67 (t, 2, J = 7 Hz, allyl), 0.68–1.08 and 1.08–1.90 (13, remainder of side chain).

Diphenyl-(1-methyl-1-heptenyl)phosphine Oxide.—A mixture of 0.5 g (0.66 mmol) of **2d** (X = Br) and 15 ml of 5% sodium hydroxide was refluxed 30 min. The mixture was cooled and extracted with ether. The ether layer was washed with water, dried (Na_2SO_4), and stripped to leave an oil which was distiled at 0.25 mm: bp 192–193°; ir ($CHCl_3$) 6.16 (C=C), 7.00 (phenyl P), 8.54 (P=O), 8.93 μ (P+); nmr ($CDCl_3$) δ 7.30–7.65 and 7.65–7.97 (10, aromatic), 6.29 (d of t, 1, J_{PH} = 21 Hz, J_{HH} = 7 Hz, vinyl), 2.02–2.50 (2, allyl CH_2), 1.87 (d, 3, J_{PH} = 13 Hz, allyl CH_3), 0.68–1.08 and 1.08–1.63 (11, side chain).

Anal. Calcd for $C_{20}H_{25}OP$: C, 76.94; H, 8.01. Found: C, 76.26; H, 8.03.

Registry No.—**1a**, X = Br, 21557-88-0; **1a**, X = picrate, 21557-89-1; **1a**, X = Br_3, 21557-90-4; **1b**, X = Br, 21557-91-5; **1c**, X = Br, 21577-58-2; **1c**, X = picrate, 21577-59-3; **1f**, X = Br, 21620-46-2; **1g**, X = Cl, 21557-92-6; **1g**, X = picrate, 21577-60-6; **2a**, X = Br, 21557-93-7; **2a**, X = picrate, 21557-94-8; **2b**, X = Br, 21557-95-9; **2b**, X = picrate, 21557-96-0; **2b**, X = Cl, 21557-97-1; **2b**, X = I, 21557-98-2; **2b**, X = $OCOCF_3$, 21620-47-3; **2c**, X = Br, 21557-99-3; **2c**, X = I, 21558-00-9; **2c**, X = Br_3, 21558-01-0; **2c**, X = picrate, 21558-02-1; **2d**, X = Br, 21558-03-2; **2d**, X = picrate, 21558-04-3; **2e**, X = Br, 21558-05-4; **2e**, X = picrate, 21558-06-5; **2f**, X = Cl, 21558-07-6; **2g**, X = Cl, 21558-08-7; **2g**, X = picrate, 21558-09-8; **3a**, 6224-94-8; **3b**, 20446-24-6; **3c**, 21558-12-3; **3d**, 21577-61-7; **3e**, 21558-13-4; **3f**, 21543-66-8; **3g**, 21543-67-9; **4a**, X = Br (phosphine), 21543-68-0; **4a**, X = Br (oxide), 21543-69-1; **4b**, X = Br (phosphine), 21543-70-4; **4b**, X = Br (oxide), 21543-71-5; **4b**, X = I (hydriodide), 21543-72-6; **4d**, X = Br (phosphine), 21543-73-7; **4d**, X = Br (oxide), 21543-74-8; **6f**, 21543-75-9; **6f**, dipicrate,

21543-76-0; diphenyl(1-methyl-1-heptenyl)phosphine oxide, 21543-77-1.

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Michael Addition of Grignard Reagents to Alkynyl-1-phosphine Sulfides

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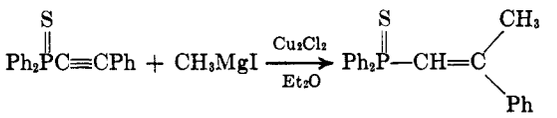
Michael addition of Grignard reagents to *t*-alkynyl-1-phosphine sulfides occurs in the presence of cuprous chloride. A variety of examples of this new reaction are described. The structures of the resulting vinylphosphine sulfides and oxides were elucidated using proton nmr.

Michael addition of a Grignard reagent to α,β-unsaturated carbonyl compounds in the presence of cuprous chloride is well established.[1] This reaction has not been extended to α,β-unsaturated phosphoryl and thiophosphoryl systems.

We wish to report the Michael addition of Grignard reagents to alkynyl-1-phosphine sulfides. When diphenyl(phenylethynyl)phosphine sulfide[2] was treated with excess methylmagnesium iodide in the presence of an equimolar amount of cuprous chloride, diphenyl-1-(2-phenylpropenyl)phosphine sulfide was isolated (eq 1).

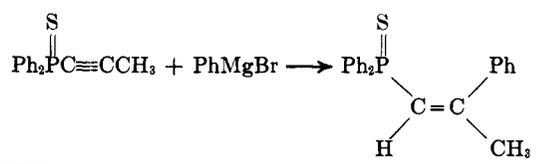


(1)

Reduction of the amount of cuprous chloride led to greatly reduced yields of product. Substituents on the phosphorus and alkynyl group were varied, and the reaction was found to be general. The reaction was extended to alkynyl-1-phosphine oxides. Diphenyl-1-butynylphosphine oxide[3] successfully added ethylmagnesium bromide under these conditions. These results are summarized in Table I.

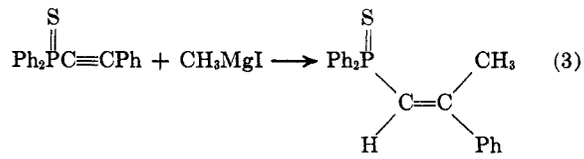
Alkynyl-1-phosphines are not alkylated even in the presence of cuprous chloride. Alkenyl-1-phosphine sulfides[4] will not alkylate.

The stereochemistry of this addition is not yet known and although *trans* addition might be expected, as in the addition of lithium aluminum hydride,[4] the results obtained in two cases do not justify this conclusion. If *trans* addition occurred, the products obtained from the reaction of phenylmagnesium bromide with diphenyl-1-propynylphosphine sulfide (eq 2) and the



(2)

reaction of methylmagnesium iodide with diphenyl(phenylethynyl)phosphine sulfide (eq 3) would be



(3)

expected to yield stereoisomers (detectable in their nmr spectra because of the proximity of the thiophosphoryl group to the allyl methyl group). The melting point, mixture melting point, and ir and nmr spectra of the two products were identical.

The mechanism of addition, the nature of the copper catalysis, and the stereochemistry of the products are now being studied.

Experimental Section

General Procedure. The Grignard reagent was prepared in three- to sevenfold excess in ether. The alkynyl-1-phosphine sulfide was then added in one portion followed by at least 1 equiv of cuprous chloride and the mixture refluxed 4–6 hr. A normal workup followed, using ammonium chloride solution and water, and the ether was stripped from the dried solution to leave the crude product. Recrystallizations from methanol or distillations produced the analytical samples. Physical constants and spectra of the products are as follows.

Dimethyl-1-(2-methylbutenyl)phosphine sulfide had bp 74–75° (0.30 mm). The ir spectrum ($CHCl_3$) showed bands at 5.90, 6.25, and 10.68 μ. The nmr spectrum ($CDCl_3$) displayed the vinyl proton as a crude doublet (J = 25 cps) at δ 5.62 (1 H), the methylenes of the ethyl group as a rough quartet (J = 7 cps) at 2.70 (2 H), the allyl methyl group as a close multiplet at 2.10–2.25 (3 H), the phosphorus methyls as a doublet (J = 13 cps) at 1.85 (6 H), and the terminal methyl hydrogens of the ethyl group as two triplets (J = 7 cps) at 1.07 and 1.14 (3 H).

Anal. Calcd for $C_7H_{15}PS$: C, 51.82; H, 9.32; P, 19.09; S, 19.76. Found: C, 51.76; H, 9.28; P, 19.23; S, 19.61.

Dimethyl-1-(2-ethylbutenyl)phosphine sulfide had bp 81–83° (0.2 mm). The ir spectrum ($CHCl_3$) showed significant absorptions at 6.19, 10.60, and 10.85 μ. The nmr spectrum exhibited the vinyl proton as a crude doublet (J = 24 cps) at δ 5.60 (1 H), the allyl methylenes as two crude quartets (J = 7.5 cps) at δ 2.61 and 2.22 with the upfield peak beneath part of the phosphorus methyls doublet (J = 13 cps) at δ 1.82 (10 H together), and the terminal methyl protons as two triplets (J = 7.5 cps) at δ 1.05 and 1.12 (6 H).

Anal. Calcd for $C_8H_{17}PS$: C, 54.51; H, 9.72; P, 17.57; S, 18.19. Found: C, 54.61; H, 9.66; P, 17.67; S, 18.14.

Dimethyl-1-(2-phenylbutenyl)phosphine sulfide had mp 104–106°. The ir spectrum ($CHCl_3$) showed bands at 6.27, 10.58,

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