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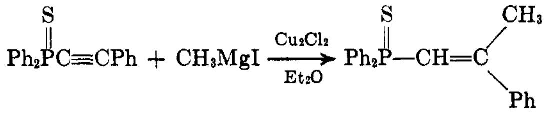
Michael addition of Grignard reagents to *t*-alkynyl-1-phosphine sulfides occurs in the presence of cuprous chloride. A variety of examples of this new reaction are described. The structures of the resulting vinylphosphine sulfides and oxides were elucidated using proton nmr.

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).

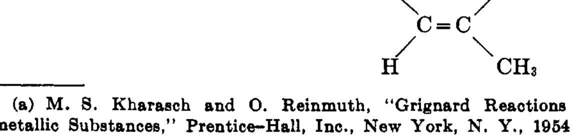


$$Ph_2\overset{\overset{S}{\|}}{P}C{\equiv}CPh + CH_3MgI \xrightarrow[Et_2O]{Cu_2Cl_2} Ph_2\overset{\overset{S}{\|}}{P}{-}CH{=}C(CH_3)Ph \qquad (1)$$

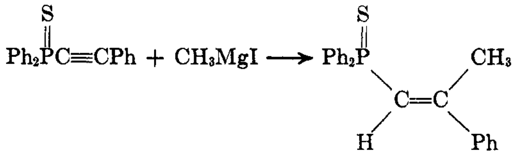
Reduction of the amount of cuprous chloride led to greatly reduced yields of product. Substituents on the phosphorus and alkynyl group were varied, and the reaction was found to be general. The reaction was extended to alkynyl-1-phosphine oxides. Diphenyl-1-butynylphosphine oxide[3] successfully added 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 reaction of methylmagnesium iodide with diphenyl(phenylethynyl)phosphine sulfide (eq 3) would be 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.



$$Ph_2\overset{\overset{S}{\|}}{P}C{\equiv}CCH_3 + PhMgBr \longrightarrow (Ph_2\overset{\overset{S}{\|}}{P})(H)C{=}C(Ph)(CH_3) \qquad (2)$$



$$Ph_2\overset{\overset{S}{\|}}{P}C{\equiv}CPh + CH_3MgI \longrightarrow (Ph_2\overset{\overset{S}{\|}}{P})(H)C{=}C(CH_3)(Ph) \qquad (3)$$

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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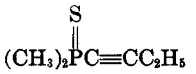
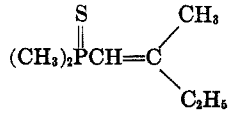
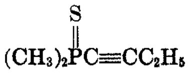
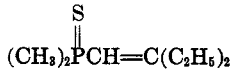
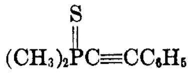
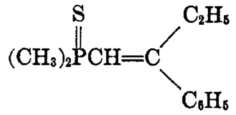
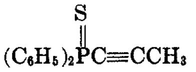
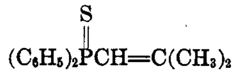
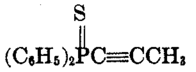
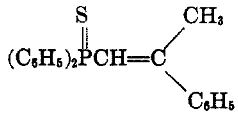
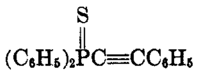
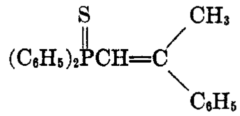
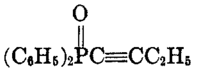
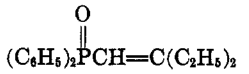
(1) (a) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, p 219; (b) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966).

(2) K. Issleib and G. Harzfeld, *Chem. Ber.*, **95**, 268 (1962).

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

(4) A. M. Aguiar, J. R. S. Irelan, and N. S. Bhacca, *J. Org. Chem.*, in press.

TABLE I

Substrate	Grignard reagent	Product	Yield, %
 $(CH_3)_2\overset{S}{\overset{\|}{P}}C\equiv CC_2H_5$	CH_3MgI	 $(CH_3)_2\overset{S}{\overset{\|}{P}}CH{=}C\begin{matrix}\diagup CH_3\\ \diagdown C_2H_5\end{matrix}$	85
 $(CH_3)_2\overset{S}{\overset{\|}{P}}C\equiv CC_2H_5$	C_2H_5MgBr	 $(CH_3)_2\overset{S}{\overset{\|}{P}}CH{=}C(C_2H_5)_2$	87
 $(CH_3)_2\overset{S}{\overset{\|}{P}}C\equiv CC_6H_5$	C_2H_5MgBr	 $(CH_3)_2\overset{S}{\overset{\|}{P}}CH{=}C\begin{matrix}\diagup C_2H_5\\ \diagdown C_6H_5\end{matrix}$	95
 $(C_6H_5)_2\overset{S}{\overset{\|}{P}}C\equiv CCH_3$	CH_3MgI	 $(C_6H_5)_2\overset{S}{\overset{\|}{P}}CH{=}C(CH_3)_2$	98
 $(C_6H_5)_2\overset{S}{\overset{\|}{P}}C\equiv CCH_3$	C_6H_5MgBr	 $(C_6H_5)_2\overset{S}{\overset{\|}{P}}CH{=}C\begin{matrix}\diagup CH_3\\ \diagdown C_6H_5\end{matrix}$	97
 $(C_6H_5)_2\overset{S}{\overset{\|}{P}}C\equiv CC_6H_5$	CH_3MgI	 $(C_6H_5)_2\overset{S}{\overset{\|}{P}}CH{=}C\begin{matrix}\diagup CH_3\\ \diagdown C_6H_5\end{matrix}$	81
 $(C_6H_5)_2\overset{O}{\overset{\|}{P}}C\equiv CC_2H_5$	C_2H_5MgBr	 $(C_6H_5)_2\overset{O}{\overset{\|}{P}}CH{=}C(C_2H_5)_2$	92

and 10.83 μ. The nmr spectrum ($CDCl_3$) displayed the phenyl protons as a singlet at δ 7.41 (5 H), the vinyl proton as a crude doublet (J = 19 cps) at 5.96 (1 H), the allyl methylenes as a crude quartet (J = 7 cps) at 2.51, the phosphorus methyls as a doublet (J = 13 cps) at 1.44, and the terminal methyl group as a broadened triplet (J = 7 cps) at 1.06 (3 H).

Anal. Calcd for $C_{12}H_{17}PS$: C, 64.26; H, 7.64; P, 13.81; S, 14.29. Found: C, 64.06; H, 7.62; P, 13.73; S, 14.34.

Diphenyl-1-(2-methylpropenyl)phosphine sulfide had mp 112.5–113.5°. The ir spectrum ($CHCl_3$) displayed bands at 6.15, 6.95, 9.06, and 11.52 μ. The nmr spectrum ($CDCl_3$) showed a complex phenyl region at δ 7.4–8.2 (10 H), the vinyl hydrogen as a crude doublet (J = 24 cps) at 6.11 (1 H), and the methyl hydrogens as two close multiplets at 1.99–2.10 and 1.88–1.99 (6 H).

Anal. Calcd for $C_{16}H_{17}PS$: C, 70.56; H, 6.29; P, 11.37; S, 11.77. Found: C, 70.37; H, 6.13; P, 11.26; S, 11.79.

Diphenyl-1-(2-phenylpropenyl)phosphine sulfide had mp 127.5–128.5°. The ir spectrum ($CHCl_3$) displayed bands at 6.28, 6.97, and 9.10 μ. The nmr spectrum ($CDCl_3$) showed a complex phenyl region of two multiplets at δ 7.2–7.7 and 7.7–8.2 (15 H), the vinyl proton as a weak doublet (J = 21 cps) at 6.58 (1 H), and the methyl protons as a close multiplet at 2.25–2.40 (3 H).

Anal. Calcd for $C_{21}H_{19}PS$: C, 75.42; H, 5.73; P, 9.26; S, 9.59. Found: C, 75.60; H, 5.64; P, 9.27; S, 9.51.

Diphenyl-1-(2-ethylbutenyl)phosphine oxide had mp 81.5–83.0°. The ir spectrum ($CHCl_3$) showed bands at 6.21, 6.96, 8.52, and 8.92 μ. The nmr spectrum ($CDCl_3$) displayed a complex aromatic region at δ 7.35–8.05 (10 H), the vinyl hydrogen as a crude doublet (J = 25 cps) at 5.91 (1 H), the methylene protons as a group of six rough peaks at 2.10–2.90 (4 H), and the methyl groups as two triplets (J = 7 cps) at 0.94 and 1.10 (6 H).

Anal. Calcd for $C_{18}H_{21}OP$: C, 76.04; H, 7.44; P, 10.89. Found: C, 75.97; H, 7.36; P, 10.95.

Registry No.—Dimethyl-1-(2-methylbutenyl)phosphine sulfide, 21544-74-1; dimethyl-1-(2-ethylbutenyl)-phosphine sulfide, 21544-75-2; dimethyl-1-(2-phenylbutenyl)phosphine sulfide, 21544-76-3; diphenyl-1-(2-methylpropenyl)phosphine sulfide, 21544-77-4; diphenyl-1-(2-phenylpropenyl)phosphine sulfide, 21544-78-5; diphenyl-1-(2-ethylbutenyl)phosphine oxide, 21544-79-6.

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