Oxidation of 1-Octene.—A solution of 11.2 g of 1-octene, 50 ml of degassed glacial acetic acid, and 3.24 g of $K_6Co_2(CN)_{10}O_2$ was heated to 80–85° under nitrogen for 24 hr. After reaction iodide titration indicated that no active oxygen remained. Vpc analysis of the reaction mixture showed a 26% yield of 1,2-octanediol diacetate which was isolated by preparative vpc and identified by its ir and nmr spectra. Only traces of other products were detected by vpc.

Reduction of Sodium Methacrylate.—The reduction of sodium methacrylate was carried out by reacting 9.8 g of KCN, 7.1 g of $CoCl_2 \cdot 6H_2O$, and 3.2 g of sodium methacrylate in 200 ml of degassed water at 100° for 3 hr in a 300-ml Magnedrive autoclave. After reaction a portion of the reaction mixture was acidified and analyzed by vpc. A 45% yield of isobutyric acid was found. The yellow reaction mixture gave uv maxima at 258 and 310 mμ, corresponding to the reported absorptions for $K_3Co(CN)_6$.[7] A pink precipitate that formed during reaction was identified as $Co(OH)_2$ by its X-ray diffraction pattern.

Registry No.—**1,** 23733-07-5; **2,** 15415-02-8; allyl alcohol, 107-18-6; 1-octene, 111-66-0; sodium methacrylate, 5536-61-8.

Acknowledgments.—The authors wish to express their gratitude to Dr. Thomas Coffield for his stimulating interest and helpful suggestions during the course of this work.

A Convenient Synthesis of 1-Alkynylphosphonates

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Interest in the preparation of 1-alkynylphosphonates (**3**) was derived from our study of nucleophilic additions to carbon–carbon triple bonds activated by phosphorus(V) groups.[2,3] A literature survey on the preparation of **3** showed that some of the methods reported involve the preparation of explosive alkynyl bromides,[4–6] while other methods are either limited in scope[7] or give low overall yields.[8]

We wish to report a versatile synthesis of **3** starting from alkynylmagnesium bromides (**1**) and dialkyl or diphenyl phosphorochloridates (**2**) (eq 1).

$$\underset{\mathbf{1}}{RC\equiv CMgBr} + \underset{\mathbf{2}}{ClP(O)(OR^1)_2} \longrightarrow \underset{\mathbf{3}}{RC\equiv CP(O)(OR^1)_2} \qquad (1)$$

$$R = \text{alkyl, cycloalkyl, aryl;}\ R^1 = \text{alkyl, aryl}$$

Some of the compounds **3** produced in this manner are listed in Table I.

The success of this method is easily explained by the reasonable assumption that the chloride ion is more easily displaced than the alkoxide and the phenoxide ion.[9] It is worthwhile to mention that in the preparation of **3i**, we observed traces of phenol in the foreruns of the distillate.

Experimental Section

General Procedure.—Alkynylmagnesium bromide was prepared by stirring 0.05 mol of the alkyne with 0.05 mol of ethylmagnesium bromide in 125 ml of ether at room temperature for 1–2 hr until no more ethane evolved. Dialkyl or diphenyl phosphorochloridate was dissolved in 70 ml of ether and cooled to 0°, and the alkynylmagnesium bromide was added dropwise with continuous stirring. The reaction mixture was stirred at 0° for 1 hr and then at room temperature for 1 hr. Saturated aqueous ammonium chloride solution (100 ml) was added slowly and the phases were separated. The aqueous layer was extracted with ether, the combined ether extract was dried ($MgSO_4$) and evaporated, and the resulting oil was distilled under reduced pressure.

Commercially available diethyl and diphenyl phosphorochloridates were used while dimethyl phosphorochloridate was prepared by passing Cl_2 through a cold solution of dimethyl phosphite in CCl_4.

The ir spectra ($CHCl_3$) of all the compounds **3** listed in Table I show a significant absorption in the region of 4.50–4.60 μ ($C\equiv C$); nmr ($CDCl_3$) **3a–h**, doublet of quartets ($J_{HH} = 7$, $J_{PH} = 9$ Hz, δ 4.15–4.20, CH_2O); **3i**, doublet ($J_{PH} = 5$ Hz, δ 1.75, CH_3); **3j**, doublet ($J_{PH} = 13$ Hz, δ 3.88, CH_3O).

TABLE I

1-ALKYNYLPHOSPHONATES **3**

Series	R	R^1	Bp, °C (mm)	Yield, %	Calcd, % C	Calcd, % H	Calcd, % P	Found, % C	Found, % H	Found, % P
a	CH_3	C_2H_5	82–83 (0.30)[a]	76						
b	n-C_3H_7	C_2H_5	115 (0.20)	59	52.94	8.39	15.16	52.77	8.25	15.04
c	n-C_4H_9	C_2H_5	96 (0.10)[a]	64						
d	n-C_6H_{13}	C_2H_5	133 (0.57)[a]	52						
e	C_6H_5	C_2H_5	132 (0.10)[a]	53						
f	$C_6H_5CH_2CH_2$	C_2H_5	145 (0.05)	60	63.15	7.19	11.63	63.02	7.36	11.80
g	C_6H_{11}	C_2H_5	130 (0.55)	51	59.01	8.67	12.68	58.65	8.86	12.76
h	C_5H_9	C_2H_5	134 (0.90)	70	57.38	8.32	13.45	56.61	8.43	12.89
i	CH_3	C_6H_5	162–163 (0.10)	74	66.78	4.81	11.38	66.04	4.72	11.04
j	n-C_3H_7	CH_3	83 (0.10)	57	47.73	7.44	17.58	47.36	7.46	17.61

[a] Reference 6.

Registry No.—**3a,** 1067-88-5; **3b,** 7579-98-8; **3c,** 3450-61-1; **3d,** 3450-66-6; **3e,** 3450-67-7; **3f,** 30238-19-8; **3g,** 30238-20-1; **3h,** 30238-21-2; **3i,** 3095-09-8; **3j,** 30238-23-4.

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A Convenient Synthesis of Dialkyl Alkynyl-1-thiophosphonates

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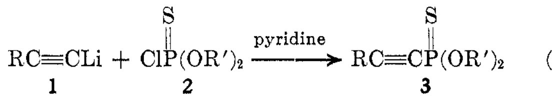
Dialkyl alkynyl-1-thiophosphonates (**3**) represent a new class of phosphorus(V) esters which have not been described in the literature to date. We now wish to report a versatile, one-step synthesis of compounds of type **3** by the reaction of dialkyl phosphorochloridothionates (**2**) with lithium alkynylides (**1**) in the presence of a catalytic amount of pyridine (eq 1).



$$\underset{\mathbf{1}}{\mathrm{RC{\equiv}CLi}} + \underset{\mathbf{2}}{\mathrm{Cl}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{P}}(\mathrm{OR'})_2} \xrightarrow{\text{pyridine}} \underset{\mathbf{3}}{\mathrm{RC{\equiv}C}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{P}}(\mathrm{OR'})_2} \qquad (1)$$

R = alkyl, cycloalkyl, phenyl; R′ = alkyl

The compounds **3** prepared by this method are listed in Table I together with their boiling points, yields, and chemical analyses. This method for the preparation of **3** is based upon the reasonable assumption that the chloride ion is much more easily displaced than the alkoxide ion.[2]

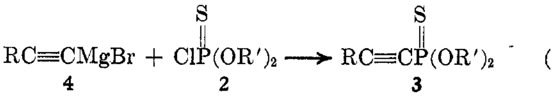
TABLE I

DIALKYL ALKYNYL-1-THIOPHOSPHONATES (**3**)

Series	R	R¹	Bp, °C (mm)	Yield, %	Calcd, % C	H	P	S	Found, % C	H	P	S
a	CH_3	C_2H_5	82–83 (0.30)	36	43.74	6.82	16.11	16.68	43.89	6.73	16.16	16.76
b	n-C_3H_7	C_2H_5	95–96 (0.10)	61	49.08	7.78	14.06	14.55	49.27	7.56	13.95	14.55
c	n-C_4H_9	C_2H_5	94 (0.07)	66	51.26	8.17	13.22	13.68	51.46	7.96	13.47	13.72
d	n-C_5H_{11}	C_2H_5	101 (0.07)	68	53.21	8.52	12.47	12.91	53.26	8.42	12.41	12.91
e	n-C_6H_{13}	C_2H_5	130 (0.20)	79	54.94	8.84	11.80	12.22	55.15	9.01	11.98	12.45
f	n-C_7H_{15}	C_2H_5	121 (0.07)	64	56.50	9.12	11.20	11.61	56.78	9.24	11.20	11.69
g	$C_6H_5CH_2CH_2$	C_2H_5	135 (0.08)	52	59.56	6.78	10.97	11.36	59.48	6.84	11.23	11.13
h	C_5H_9	C_2H_5	110 (0.12)	81	53.64	7.78	12.57	13.02	53.80	7.61	12.60	13.19
i	C_6H_{11}	C_2H_5	134 (0.45)	74	55.36	8.13	11.90	12.32	55.25	8.24	11.95	12.60
j	C_6H_5	C_2H_5	134–135 (0.15)	52	56.68	5.95	12.18	12.61	57.07	6.11	12.15	12.63
k	C_6H_5	CH_3	119 (0.20)	35	53.09	4.90	13.69	14.17	53.07	5.00	13.77	14.27

The ir spectra of **3a–k** display significant absorption in the region of 4.50–4.60 μ (C≡C). The nmr spectra of **3a–j** exhibit a doublet of quartets ($J_{HH} = 7$, $J_{PH} = 11$ Hz) at δ 4.08–4.25 due to methylenes from the *O*-ethyl groups; compound **3k** displays a doublet ($J_{PH} = 15$ Hz) at δ 3.82 due to the methyl groups. All other proton resonances are in full agreement with the assigned structures.

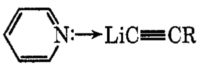
Initial attempts at preparing **3** in tetrahydrofuran (THF) and in ether by the treatment of **2** with alkynylmagnesium bromides (**4**) produced the desired product in low yields (eq 2).



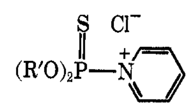
$$\underset{\mathbf{4}}{\mathrm{RC{\equiv}CMgBr}} + \underset{\mathbf{2}}{\mathrm{Cl}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{P}}(\mathrm{OR'})_2} \longrightarrow \underset{\mathbf{3}}{\mathrm{RC{\equiv}C}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{P}}(\mathrm{OR'})_2} \qquad (2)$$

It was found that the yield of **3** from the reaction of **1** with **2** can be maximized in mixed THF–ether solvent by utilizing a catalytic amount of pyridine.

The catalytic action of pyridine may be due to its ability to coordinate with lithium, thereby increasing the nucleophilicity of the alkynylide moiety through intermediates such as **5**. Pyridine may be increasing the electrophilicity of phosphorus through formation of intermediate **6**.



5



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We favor major contribution of **5** because, although the addition of pyridine increased the yield of **3** when the lithium alkynylides (**1**) were used (eq 1), it failed to have any effect on the alkynylmagnesium bromide (**4**) reaction (eq 2). Moreover, the acceleration of the rates of organolithium reactions resulting from low concentrations of amines has been well established. The effect has been attributed to complex formation which labilizes the carbon–lithium bond.[3]

Experimental Section

All the reactions were run under nitrogen, from the introduction of the 1-alkyne until the addition of water. Tetrahydrofuran was dried over calcium hydride for 3–4 days and distilled. The nmr spectra were determined in deuteriochloroform solution, with tetramethylsilane as an internal standard, on a Varian A-60 spectrometer. Chemical analyses were performed by Geller Microanalytical Laboratories, Saddle River, N. J. Commercially available dialkyl phosphorochloridothionates (**2**) were used.

Preparation of Dialkyl Alkynyl-1-thiophosphonates. General Procedure.—The alkyne (0.05 mol) was dissolved in a mixture of 50 ml of ether and 25 ml of THF and cooled to 0°. A hexane solution of *n*-butyllithium (0.05 mol, 32.5 ml of 1.6 *M* solution, Foote Chemical Co.) was slowly added with continuous stirring to obtain a fine suspension of lithium alkynylide.[4] Two drops of

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