Acknowledgment.—We wish to acknowledge the National Institutes of Health for support of this work under Grant GM-16828 and the National Science Foundation under Grant GP-10739.

A Convenient Synthesis of Dialkyl Alkynyl-1-thiophosphonates

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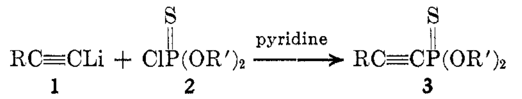
Received January 7, 1971

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).



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

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]

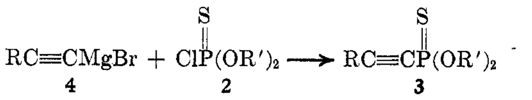
TABLE I

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

Series	R	R¹	Bp, °C (mm)	Yield, %	Calcd, % C	Calcd, % H	Calcd, % P	Calcd, % S	Found, % C	Found, % H	Found, % P	Found, % 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 ($J_{\mathrm{HH}} = 7$, $J_{\mathrm{PH}} = 11$ Hz) at δ 4.08–4.25 due to methylenes from the *O*-ethyl groups; compound **3k** displays a doublet ($J_{\mathrm{PH}} = 15$ Hz) at δ 3.82 due to the methyl groups. All other proton resonances are in full agreement with the assigned structures.

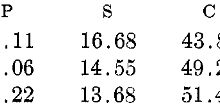
Initial attempts at preparing **3** in tetrahydrofuran (THF) and in ether by the treatment of **2** with alkynylmagnesium bromides (**4**) produced the desired product in low yields (eq 2).



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

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**.



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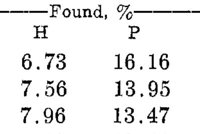

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We favor major contribution of **5** because, although the addition of pyridine increased the yield of **3** when the lithium alkynylides (**1**) were used (eq 1), it failed to have any effect on the alkynylmagnesium bromide (**4**) reaction (eq 2). 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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[1] Author to whom correspondence should be addressed.

[2] A. M. Aguiar, J. R. S. Irelan, C. J. Morrow, J. P. John, and G. W. Prejean, *J. Org. Chem.*, **34**, 2684 (1969).

[3] F. G. A. Stone and R. West, "Organometallic Chemistry," Vol. 3, Academic Press, New York, N. Y., 1965, p 392.

[4] T. F. Rutledge, "Acetylenic Compounds," Reinhold, New York, N. Y., 1968, p 68.

pyridine were added and this suspension was slowly added to a solution of **2** (0.05 mol) in 50 ml of ether at 0°. The reaction mixture was stirred at 0° for 1 hr and then at room temperature for 5–6 hr. The reaction mixture was cooled in an ice bath and 100 ml of saturated aqueous ammonium chloride solution was slowly added. The phases were separated and the aqueous layer was extracted twice with 50-ml portions of ether. The combined ethr extract was dried ($MgSO_4$), filtered, and evaporated. The resultant oil was distilled at reduced pressure to yield the alkynyl-1-thiophosphonates **3**.

In the preparation of **3k** ($R = C_6H_5$, $R' = CH_3$) only ether was used as a solvent.

Registry No.—**3a**, 20553-76-8; **3b**, 30238-04-1; **3c**, 30238-05-2; **3d**, 30238-06-3; **3e**, 30238-07-4; **3f**, 30238-08-5; **3g**, 30238-09-6; **3h**, 30238-10-9; **3i**, 30238-11-0; **3j**, 30238-12-1; **3k**, 30238-13-2.

Acknowledgment.—We wish to acknowledge the National Institutes of Health for support of this work under Grant GM-16828 and the National Science Foundation under Grant GP-10739.

Reactions of Lithium Dimethylcarbamoylnickel Carbonylate

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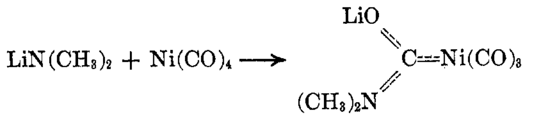
Received December 21, 1970

In a previous paper[1] we have reported the formation of an air-sensitive anionic carbamoylnickel complex, $Li[(CH_3)_2NCONi(CO)_3]$ (**1**), by the addition of lithium dimethylamide to nickel carbonyl and the reaction of **1** with phenylacetylene to yield 2-phenyl-*N*,*N*,*N'*,*N'*-tetramethylsuccinamide and *N*,*N*-dimethylcinnamamide under mild conditions. More recently, anionic organometal carbonylates have been shown to be effective nucleophilic reagents in organic syntheses and several types of new reactions have been established: *e.g.*, nucleophilic acylation of organic halides[2,3] and conjugated enones[4] using lithium acyl metal carbonylates derived from organolithium compounds and mononuclear metal carbonyls, and alkoxycarbonylation of organic halides[5] using nickel carbonyl and potassium alkoxide.

In this paper, we wish to report the reaction of lithium dimethylcarbamoylnickel carbonylate (**1**) as a nucleophilic carbamoylation reagent. The reaction of alkyl carbamoyl chloride with carbanion has been well known as a method for electrophilic carbamoylation accompanying a carbon–carbon bond formation.[6] The anionic carbamoyl group may show different behavior than the cationic one and give rise to a new type of organic reaction. Because of the difficulty in forming such a group, there are few reports on nucleophilic carbamoylation except the reaction system of biscarbamoylmercury compounds and *n*-butyllithium at very low temperature.[7]

Results and Discussion

Assumed Structure of Lithium Dimethylcarbamoylnickel Carbonylate (1).—Addition of nickel carbonyl to the white ether suspension of lithium dimethylamide yields a clear red solution without carbon monoxide evolution. The infrared spectrum of this solution shows peaks at 1973 (vs), 1954 (s) ($\nu_{C=O}$ of terminal carbonyl of the anionic complex), and 1560 cm^{-1} (m, broad) ($\nu_{C=O}$ and $\nu_{C=N}$ of the carbamoyl group bonded to nickel[8]). These data suggest that the $Ni(CO)_3$ group in **1** has C_{3v} symmetry (two infrared active terminal carbonyl vibrations) and that the carbamoyl group is bonded to nickel as a carbene type ligand (eq 1). (Recently, lithium oxydiethylaminocarbenechromium pentacarbonylate has been isolated by the analogous reaction using lithium diethylamide and chromium hexacarbonyl in ether.[9])



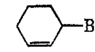
$$LiN(CH_3)_2 + Ni(CO)_4 \longrightarrow \overset{LiO}{\underset{(CH_3)_2N}{}}\!\!>C{=}Ni(CO)_3 \qquad (1)$$

Reaction of 1 with Organic Halides.—Treatment of **1** with several organic halides, RX or RCOX, in ether results in formation of the acid amides $RCON(CH_3)_2$. The examples cited in Table I illustrate the synthesis of *N*,*N*-dimethyl acid amides using the indicated reactants and reaction conditions.

TABLE I

DIMETHYLCARBAMOYLATION OF ORGANIC HALIDES

$$\underset{\mathbf{1}}{Li[(CH_3)_2NCONi(CO)_3]} + RX \text{ (or RCOX)} \longrightarrow RCON(CH_3)_2{}^{a}$$

Organic halides (RX or RCOX)	Reaction time, hr (temp, °C)	$RCON(CH_3)_2$, % yield[b]
trans-PhCH=CHBr	7 (10)	96.0
PhI	5 (37)	98.2
$PhCH_2Br$	12 (33)	64.8[c]
$CH_2{=}CHCH_2Br$	0.5 (15)	35.9[d]
	10 (20)	99.3
CH_3COCl	0.5 (22)	75.9[e]
n-C_4H_9COCl	0.5 (22)	97.1[e]
PhCOCl	5 (30)	95.6[e]

[a] Reactants ratio, $LiN(CH_3)_2:Ni(CO)_4:$halide = 1:2:2. [b] Yields were calculated based on $LiN(CH_3)_2$ used. [c] Other product, $PhCH_2N(CH_3)_2$ (33.2%). [d] Product, $CH_3CH{=}CHCON(CH_3)_2$. [e] None of $RCOCON(CH_3)_2$ was detected.

In general, the reactivity sequence of alkyl halides

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[1] S. Fukuoka, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **33**, 2973 (1968).

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[6] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," Wiley, New York, N. Y., 1953, p 576.

[7] U. Schöllkopf and F. Gerhart, *Angew. Chem., Int. Ed. Engl.*, **6**, 805 (1967).

[8] It has been reported that the neutral carbamoyl transition metal complex shows a $\nu_{C=O}$ peak (m or w) at 1535 ± 10 cm^{-1} in π-$C_5H_5Fe(CO)_2(CONR_2)$ [R. B. King, *J. Amer. Chem. Soc.*, **85**, 1918 (1963)], 1625 cm^{-1} in π-$C_5H_5Fe(CO)_2(CONHCH_3)$ [L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, **2**, 391 (1968)], 1512 cm^{-1} in *cis*-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$ [H. Behrens, E. Linder, and P. Pässler, *Z. Anorg. Allg. Chem.*, **365**, 137 (1969)], and 1598 cm^{-1} in $(n$-$C_3H_7)_2NCOCo(CO)_3(PPh_3)$ [J. Palágyi and L. Markó, *J. Organometal. Chem.*, **17**, 453 (1969)].

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