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One-Pot Synthesis of 1-Alkynylphosphonates

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ONE-POT SYNTHESIS OF 1-ALKYNYLPHOSPHONATES

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Abstract: 1-Alkynylphosphonates **3** are prepared in a one-pot procedure from diethyl phosphorochloridates **2** and alkynyllithiums **1**, which are readily generated by the reaction of 1-alkynes with *n*-BuLi.

1-Alkynylphosphonates **3** have been used to synthesize a wide variety of unsaturated and saturated functional derivatives of organophosphorus compounds.[1] A literature survey on the preparation of 1-alkynylphosphonates **3** showed that some of the methods reported involve the preparation of explosive alkynyl bromides,[2] while other methods are either limited in scope or give low overall yields.[3] Recently, we reported the preparation of 1-alkynylphosphonates by β-elimination of phosphates.[4] The most widely used method of preparation involves the reaction of alkynylmagnesium bromides with dialkyl phosphorochloridates,[5,6] but this method[5] has some limitations. One of the limitations is the formation of side products, produced by attack of the alkynylmagnesium bromides on both the chloride and the alkoxide groups of dialkyl phosphorochloridates. Herein, we

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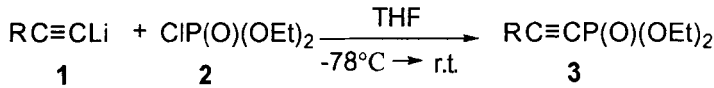
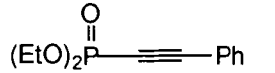
report an improved reaction which can overcome this limitation. 1-Alkynylphosphonates **3** are prepared in a one-pot procedure by reaction of diethyl phosphorochloridates **2** with alkynyllithiums **1**, which are readily generated by the reaction of 1-alkynes with *n*-BuLi (**Scheme**).



Scheme

Table. Preparation of 1-Alkynylphosphonates **3** (1~5)

entry	Product	yield, %[a]
1		82[b]
2		92[c]
3		91[c]
4		86[c]
5		82[c]

a isolated yields

b purification by distillation under reduced pressure

c purification by silica gel chromatography

The success of this method is explained by the reasonable assumption that the alkynyllithium is less nucleophilic than the alkynylmagnesium bromide and that the alkynyllithium can displace the chloride but not the alkoxide.

General Experimental Procedure

After stirring of a THF (30 ml) solution of distilled 1-alkyne **1** (10 mmol) with *n*-BuLi (10 mmol) for 1 h at -30 °C, distilled diethyl phosphorochloridate **2** (10 mmol) was added neat at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and then at room temperature for 30 min. Saturated aqueous ammonium chloride solution (20 ml) was added and the aqueous layer was extracted with ethyl ether (50 ml x 3). The combined ether extracts were dried ($MgSO_4$) and evaporated, and 1-alkynylphosphonate **3** was obtained as the only isolable product. The resulting oils were purified by silica gel column chromatography or distillation under reduced pressure (**Table**).

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