Hypervalent Iodine in Synthesis. 10. An Efficient Route to *S*-Alkynyl *O,O*-Dialkyl Phosphorodithioates

Zu-Dong Liu and Zhen-Chu Chen*

Department of Chemistry, Hangzhou University, Hangzhou, People's Republic of China

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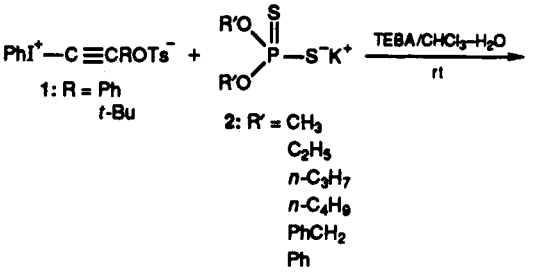
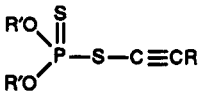
O,O-Dialkyl esters of phosphorodithioic acids are of marked interest because of their exceptional insecticidal properties and low mamalian toxicity.[1-3] Much research has been devoted to their preparation. Preparation of *S*-alkyl esters is normally not difficult, since such esters can be readily prepared by the addition of the corresponding phosphorodithioic acids to double bonds,[4-7] by the alkylation of salts of the acids with alkyl halides,[4,8] or by the reaction of thiol salts with *O,O*-dialkyl phosphorochloridothioates.[4] However, these methods are not suitable for the preparation of *S*-alkynyl *O,O*-dialkyl phosphorodithioates which have high selective activity toward acaric arthropods.[9,10]

The only known methods for the preparation of *S*-alkynyl *O,O*-dialkyl phosphorodithioates are based upon the reaction of *O,O*-dialkyl *S*-chloro phosphorodithioates with organomagnesium reagents[11] or the action of lithium alkynylides on the disulfides of *O,O*-dialkyl phosphorodithioates.[12] The first approach suffered from the disadvantage of lower yields (15–25%). Although the yields of the second approach are higher, it is deficient in some respects such as using expensive organolithium reagents, strict reaction conditions, and having to make the disulfides of *O,O*-dialkyl esters of phosphorodithioic acids by a multistep route. Clearly, a simple and convenient method for the synthesis of *S*-alkynyl *O,O*-alkyl phosphorodithioates would be highly desirable.

Our recent interest in hypervalent iodine species in organic synthesis,[13] coupled with the ready availability and high reactivity[14] of alkynylphenyliodonium salts 1, prompted us to examine the possibility of using the salts as direct alkynylating agents to synthesize *S*-alkynyl *O,O*-dialkyl phosphorodithioates 3 from potassium *O,O*-dialkyl phosphorodithioates 2. Hence, in this paper we report an efficient method for the synthesis of *S*-alkynyl *O,O*-dialkyl phosphorodithioates 3 by the reaction of alkynylphenyliodonium salts 1 with potassium *O,O*-dialkyl phosphorodithioates 2.





3a: R = Ph; R' = CH_3
b: R = Ph; R' = C_2H_5
c: R = Ph; R' = n-C_3H_7
d: R = Ph; R' = n-C_4H_9
e: R = Ph; R' = $PhCH_2$
f: R = Ph; R' = Ph
g: R = t-Bu; R' = C_2H_5
h: R = t-Bu; R' = $PhCH_2$
i: R = t-Bu; R' = Ph

Analogous to alkynylation on sulfur of sodium sulfinates,[13] the alkynylation of the potassium salts of *O,O*-dialkyl phosphorodithioates 2 with alkynylphenyliodonium salts 1 readily occurred in a single step to afford *S*-alkynyl *O,O*-dialkyl phosphorodithioates 3.

Simple stirring of the alkynylphenyliodonium salts 1 with the potassium *O,O*-dialkyl phosphorodithioates 2 in a two-phase system consisting of chloroform and water in the presence of a catalytic amount of TEBA at room temperature gave, after workup and isolation, the desired products, *S*-alkynyl *O,O*-dialkyl phosphorodithioates 3, in good yield as shown in Table I.

The products were characterized by elemental analyses (for unknown compounds) and by IR and ^1H NMR spectra. The data are summarized in Table I.

In conclusion, we have discovered a new and efficient method for the synthesis of *S*-alkynyl *O,O*-dialkyl phosphorodithioates 3. It has some advantages, such as the ease of obtaining starting materials, mild reaction conditions, simplicity of the procedure, and higher yields. Furthermore, the range of useful applications of alkynylphenyliodonium salts as an alkynylating agent in organic chemistry has been extended.

Experimental Section

General Procedure for the Preparation of *S*-Alkynyl *O,O*-Dialkyl Phosphorodithioates 3. A solution of alkynylphenyliodonium salts 1 (1 mmol) in $CHCl_3$ (15 mL) was added to the solution of potassium *O,O*-dialkyl phosphorodithioates 2 (1.5 mmol) and TEBA (0.1 mmol) in H_2O (15 mL). The mixture was stirred at room temperature for the times given in Table I. After the reaction was complete, the organic layer was separated and the water layer was extracted with $CHCl_3$ (3 × 10

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Table I. *S*-Alkynyl *O,O*-Dialkyl Phosphorodithioates 3

product	reaction time (min)	yield[a] (%)	mp (°C)[b]	molecular formula[c] or lit. bp (°C/mmHg)	^{1}H NMR, ppm ($CDCl_3$/TMS)[d]
3a: R = Ph, R′ = CH_3	20	85	oil	oil[9]	3.92 (d, 6 H, J_{HP} = 15.6), 7.10–7.37 (m, 5 H)
3b: R = Ph, R′ = C_2H_5	15	83	oil	130/0.15[11]	1.44 (t, 6 H, $J_{HH} \sim 8$, $J_{HP} < 1$), 4.23–4.53 (m, 4 H), 7.29–7.38 (m, 5 H)
3c: R = Ph, R′ = *n*-C_3H_7	30	96	oil	134/0.1[11]	1.02 (t, 6 H, J_{HH} = 7.2), 1.77–1.97 (m, 4 H), 4.09–4.29 (m, 4 H), 7.35–7.37 (m, 5 H)
3d: R = Ph, R′ = *n*-C_4H_9	20	87	oil	147/0.15[11]	0.93 (t, 6 H, J_{HH} = 6.4), 1.25–1.68 (m, 8 H), 4.21–4.41 (m, 4 H), 7.34–7.36 (m, 5 H)
3e: R = Ph, R′ = $PhCH_2$	30	91	56.0–57.5	$C_{22}H_{19}O_2PS_2$	5.20 (d, 4 H, J_{HP} = 9.6), 7.23–7.31 (m, 15 H)
3f: R = Ph, R′ = Ph	30	93	67.0–68.0	$C_{20}H_{15}O_2PS_2$	7.22 (s, 15 H)
3g: R = *t*-Bu, R′ = C_2H_5	20	94	oil	$C_{10}H_{19}O_2PS_2$	1.22 (s, 9 H), 1.40 (t, 6 H, J_{HH} = 7.2), 4.15–4.37 (m, 4 H)
3h: R = *t*-Bu, R′ = $PhCH_2$	25	89	46.5–49.0	$C_{20}H_{23}O_2PS_2$	1.15 (s, 9 H), 5.21 (d, 4 H, J_{HP} = 9.3), 7.36–7.38 (m, 10 H)
3i: R = *t*-Bu, R′ = Ph	25	95	82.0–84.0	$C_{18}H_{19}O_2PS_2$	1.26 (s, 9 H), 7.40 (s, 10 H)

[a] Yield of isolated pure product based on 1. [b] All melting point were uncorrected. [c] Satisfactory microanalyses obtained: C ± 0.23; H ± 0.25. [d] ^{1}H NMR spectra were recorded at Bruker AC-80.

mL). The combined organic layers were washed with water (3 × 20 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was recrystallized from ethanol or was chromatographed on silica gel using cyclohexane as eluent, then chloroform, to afford the *S*-alkynyl *O,O*-dialkyl phosphorodithioates **3**. All relevant data are summarized in Table I.

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Supplementary Material Available: IR spectral data for **3a–i** and results of elemental analyses of **3e–i** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.