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Synthesis of vinyloxy phosphorus monomers from the enolate of acetaldehyde

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Summary

A simple synthetic procedure for vinyloxy phosphorus monomers involves the reaction of the enolate of acetaldehyde, obtained from the cycloreversion of tetrahydrofuran in the presence of *n*-butyllithium, with chlorophosphites or phosphorochloridates leading to vinyl phosphites or vinyl phosphates, respectively, in high yield and purity.

Introduction

An efficient synthesis of unsubstituted vinyloxy phosphorus compounds is of interest because these monomers are often used for flame-retardant polymers, insecticides, and many pharmaceuticals.[1] Inspection of the literature yields many potential synthetic routes to these types of compounds, such as the Perkow reaction,[2] the use of mercurials,[3] chloroacetaldehyde,[4,5] dehydrochlorination of the corresponding 2-chloroethyl esters,[6-8] and chloroethylenecarbonate.[9]

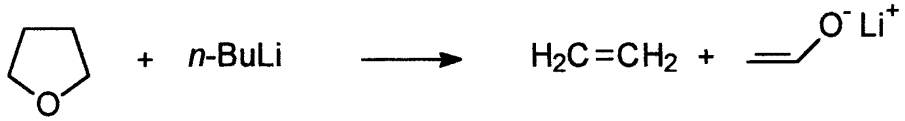
The most commonly used synthesis of unsubstituted vinyloxy phosphorus compounds is the Perkow reaction, which involves addition of a trivalent phosphorus containing at least one alkoxy group to an α-haloketone. The Perkow method is undesirable since it involves the use of anhydrous chloroacetaldehyde, which is hazardous nature and not readily available. Gross and Costisella circumvent this problem by generating chloroacetaldehyde in situ from chloroethylene carbonate in the presence of a catalytic amount of triethyl amine, followed by addition of triethyl phosphite.[10] A possible alternative involves the use of mercury salts, which presents a definite economical barrier, particularly for large scale synthesis, and poses environmental and toxicity problems. A more promising lead is found in the work of Ireland and Pfister, who reported the formation of diethyl vinyl phosphate from enolate anions formed by the reduction of α,β-unsaturated ketones by lithium ammonium.[11]

Based on this information, we decided that the lithium salt of vinyl alcohol as an intermediate was the best choice for a versatile and straightforward synthesis of a large variety of vinyloxy phosphorus compounds. Bates and coworkers generated this lithium enolate of acetaldehyde from the cycloreversion of tetrahydrofuran in the presence of *n*-butyllithium.[12] The versatility of the acetaldehyde enolate using the Bates method has been well documented. Jung and Blum demonstrated that the lithium enolate of acetaldehyde could be O-acylated, O-silylated or C-alkylated.[13] Duggan and Roberts found that acylation of this enolate with diphenyl thiocarbonate

afforded vinyl phenyl thiocarbonate in reasonable yields.[14] Using diethyl phosphorochloridate, Widlanski and co-workers generated phosphate diesters which could not be synthesized using standard phosphoramidite methodology, again demonstrating the versatility of the method employed.[15]

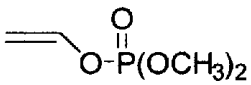
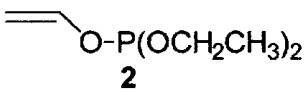
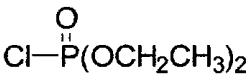
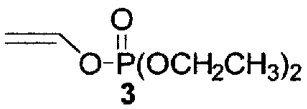
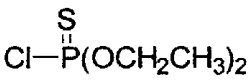
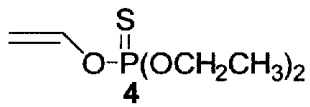
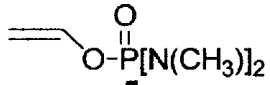
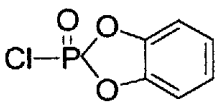
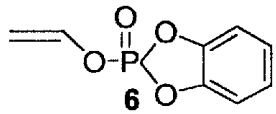
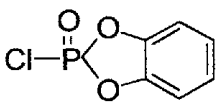
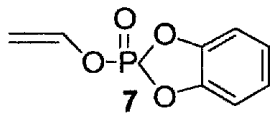
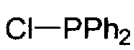
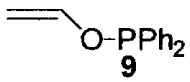
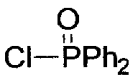
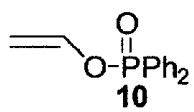
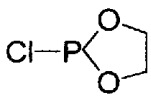
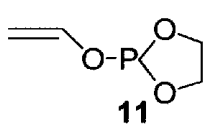
Results and Discussion

To determine the utility of the lithium enolate of acetaldehyde in the synthesis of phosphorus derivatives, its reaction with a series of chlorophosphates and chlorophosphites was investigated yielding the corresponding vinyl phosphates and vinyl phosphites respectively. The results are summarized in Table 1. High yields were obtained for all reactions and these yields remained high upon scale-up. Isolation and purification were extremely simple, namely evaporation of the excess THF followed by vacuum distillation. Elemental analysis and NMR confirmed the structure of these compounds and their purity.



In summary, we have demonstrated that enol phosphites and phosphates result from the interaction of the acetaldehyde enolate and a phosphorylating agent with very little required in terms of purification to obtain high yields. By this method we have prepared vinyl phosphites, vinyl phosphates, and vinyl thiophosphates with varying substituents. These studies have given facile access to a sufficient variety of structures so that attention can be focused on applications of vinyloxy phosphorus compounds.

Table 1. Synthesis of Vinyloxy Phosphorus Compounds

Phosphorylating agent	Vinyloxy phosphorus compound	Yield, %
	 **1**	**80**
	 **2**	**87**
	 **3**	**85**
	 **4**	**85**
	 **5**	**87**
	 **6**	**71**
	 **7**	**72**
	 **8**	**78**
	 **9**	**82**
	 **10**	**66**
	 **11**	**57**

Experimental

General

To maintain anhydrous conditions, tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. Commercially available reagents were used as received. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. Reported yields are the average of two or more runs. All NMR spectra were recorded in $CDCl_3$ or acetone-d_6 on a Varian Instruments Gemini 200 spectrometer. Infrared spectra were recorded on a Nicolet Impact 410 spectrometer. Elemental analysis was performed by Desert Analytics, Tucson, Arizona.

Typical Procedure

Dry tetrahydrofuran (50 mL, 0.61 mole) was placed in a dry three-neck, round-bottomed flask under nitrogen. *n*-Butyllithium in *n*-hexane solution (2.5M, 32.4 mL, 0.08 mole) was added using a syringe. After 3 hours stirring at room temperature under nitrogen the mixture was cooled to -50 °C followed by dropwise addition of the chlorophosphorus compound over a period of 20 min. After an additional 3 h the reaction mixture was concentrated *in vacuo* and distilled under reduced pressure using a Kugelrohr apparatus.

Dimethyl Vinyl Phosphate (1).[16-17]. 80% yield, 80-82 °C/10 mmHg. IR (NaCl, neat) 3075, 2986, 1640, 1376 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 6.62 (ddd, J= Hz), 4.89 (ddd, J= Hz), 4.59 (ddd, J= Hz), 3.80 (d, J= 11.5 Hz).

Diethyl Vinyl Phosphite (2). 87% yield, 105-107 °C/20 mmHg. IR (NaCl, neat) 3118, 2997, 1636, 1388, 1045 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 6.61 (ddd, J=6.15, 6.88, 12.67 Hz, 1H), 4.61 (dd, J=0.87, 1.10, 12.67 6.15 Hz, 1H), 3.91 (q, 4H), 1.22 (t, 6H). ^{13}C NMR (50 MHZ, $CDCl_3$) δ 143.0 (J_{CP}=5.6 Hz), 96.2 (J_{CP}=10.1 Hz), 58.9 (J_{CP}=6.0 Hz), 17.3 (J_{CP}=6.3 Hz). Anal. Calcd. for $C_6H_{13}O_3P$: C, 43.90; H, 7.98; P, 18.87. Found: C, 43.50; H, 8.12; P, 18.76.

Diethyl Vinyl Phosphate (3).[16-17] 85% yield, 94-95 °C/11 mmHg. IR (NaCl, neat) 3077, 2986, 1645, 1282 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 6.39 (ddd, J=5.95, 6.57, 13.46 Hz, 1H), 4.71 (ddd, J=1.01, 1.75, 13.46 Hz, 1H), 4.39 (ddd, J=1.75, 2.90, 5.95 Hz, 1H), 3.95 (q, 4H), 1.17 (t, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.8 (J_{CP}=5.7 Hz), 99.2 (J_{CP}=10.3 Hz), 63.9 (J_{CP}=6.1 Hz), 15.6 (J_{CP}=6.5 Hz).

Diethyl Vinyl Phosphorothioate (4). 85% yield, 82-84 °C/7.5 mmHg. IR (NaCl, neat) 3095, 2984, 1643, 1137 cm^{-1}. ^1H NMR (200 MHz, Acetone-d_6) δ 1.31 (t, 3H), 4.16 (q, 4H), 4.60 (ddd, J=1.83, 2.76, 5.89 Hz, 1H), 4.87 (ddd, J=1.05, 1.83, 13.55 Hz, 1H), 6.70 (ddd, J=5.89, 6.27, 13.55 Hz, 1H). ^{13}C NMR (50 MHz, Acetone-d_6) δ 142.2 (J_{CP}=4.9 Hz), 99.3 (J_{CP}=11.6 Hz), 64.6 (J_{CP}=5.6 Hz), 15.7 (J_{CP}=7.3 Hz). Anal. Calcd for $C_6H_{13}O_3PS$: C, 36.73; H, 6.68; S, 16.34. Found: C, 36.86; H, 6.70; S, 16.72.

O-Ethenyl-N,N,N',N'-Tetramethyl Phosphoric Diamide (5). 87% yield, 125-127

°C/20 mmHg. IR (NaCl, neat) 3069, 2929, 1640, 1303 cm^{-1}. ^{1}H NMR (200 MHz, Acetone-d_6) δ 6.61 (ddd, J=5.94, 6.92, 13.72 Hz, 1H), 4.72 (ddd, J=0.98, 1.83, 13.72 Hz, 1H), 4.41 (ddd, J=1.83, 2.91, 5.94 Hz, 1H), 2.88 (s, 3H), 2.64 (s, 3H), 2.62 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (50 MHz, Acetone-d_6) δ 144.1 (J_{CP}=4.9 Hz), 97.7 (J_{CP}=10.0 Hz), 37.20, 36.76, 36.70. Anal. Calcd for $C_6H_{15}N_2O_2P$: C, 40.4; H, 8.5; N, 15.7. Found: C, 40.3; H 8.2; N 15.7.

O-Phenylene Vinyl Phosphate (6). 71% yield, 132-134 °C/20 mmHg. IR (NaCl, neat) 3097, 2994, 1640, 1383 cm^{-1}. ^{1}H NMR (200 MHz, Actone-d_6) δ 7.15-7.35 (m, 4H), 6.74 (ddd, J=5.70, 6.39, 13.21 Hz, 1H), 5.10 (ddd, J=1.06, 1.51, 13.21 Hz, 1H), 4.84 (ddd, J=1.51, 2.57, 5.70 Hz, 1H). ^{13}C NMR (50 MHz, Acetone-d_6) δ 144.6, 142.3 (J_{CP}=7.2 Hz), 125.2, 124.2, 113.4 (J_{CP}=13.4 Hz), 112.9 (J_{CP}=12.7 Hz), 102.8 (J_{CP}=10.5 Hz). HRMS (matrix, NBA): calcd. for $C_8H_7O_4P•H^+$ 199.0082, found 199.0160.

O-Phenylene Vinyl Phosphite (7). 72% yield, 117-119 °C/15 mmHg. IR (NaCl, neat) 3067, 1634, 1331 cm^{-1}. 1H NMR (200 MHz, Acetone-d_6) δ 7.01-7.36 (m, 4H), 6.33 (ddd, J=5.82, 6.94, 13.59 Hz, 1H), 4.70 (ddd, J=1.10, 1.54, 13.57 Hz, 1H), 4.40 (ddd, J=1.54, 2.97, 5.82 Hz, 1H). ^{13}C NMR (50 MHz, Acetone-d_6) δ 145.7, 142.0 (J_{CP}=3.9 Hz), 125.4, 124.1, 114.8, 113.2, 100.8 (J_{CP}=7.2 Hz). HRMS (matrix, NBA): calcd. for $C_8H_7O_3P•H^+$ 183.0133, found 183.0211.

O-Ethynyl-N,N,N',N'-Tetraethyl Phosphite Diamine (8). 78% yield, 110-114 °C/18 mmHg. IR (NaCl, neat) 3091, 2098, 1642, 1330. ^{1}H NMR (200 MHz, Acetone-d_6) δ 6.46 (ddd, J=5.95, 6.31, 13.71 Hz, 1H), 4.44 (dd, J=1.50, 13.71 Hz, 1H), 4.11 (ddd, J=1.50, 2.93, 5.95 Hz, 1H), 2.88-3.17 (m, 8H), 1.04 (t, 12H). ^{13}C NMR (50 MHz, Acetone-d_6) δ 147.7 (J_{CP}=18.6 Hz), 93.5 (J_{CP}=10.7 Hz), 40.2, 39.8, 15.3 (J_{CP}=2.8 Hz). Anal. Calcd for $C_{10}H_{23}N_2OP$: C, 55.0; H, 10.6; N, 12.8. Found: C, 54.6; H, 10.6; N, 12.8.

Diphenyl Vinyl Phosphite (9). 82% yield from gas chromatography. Attempted isolation of this product resulted in the formation of oligomers.

Diphenyl Vinyl Phosphine Ester (10). 66% yield, 147-149 °C/15 mmHg. IR (NaCl, neat) 3058, 1639, 1235. ^{1}H NMR (200 MHz, Acetone-d_6) δ 7.88-7.99 (m, 4H), 7.51-7.59 (m, 6H), 6.76 (ddd, J=5.94, 7.97, 13.60 Hz, 1H), 5.05 (dd, J=1.83, 13.60 Hz, 1H), 4.63 (dd, J=1.83, 5.94 Hz, 1H). ^{13}C NMR (50 MHz, Acetone-d_6) δ 142.1 (J_{CP}=6.3 Hz), 133.2 (J_{CP}=7.0 Hz), 132.1 (J_{CP}=10.2 Hz), 130.6, 129.3 (J_{CP}=13.0 Hz), 100.6 (J_{CP}=9.0 Hz). Anal. Calcd. for $C_{14}H_{13}O_2P$: C, 68.9; H, 5.4. Found: C, 69.0; H, 5.4.

Vinyl-1,3,2-dioxaphosphite (11). 57% yield, 110-112 °C/20 mmHg. IR (NaCl, neat) 3060, 2904, 1639, 1313 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.45 (ddd, J=5.58, 6.22, 13.56 Hz, 1H), 4.63 (dd, J=1.42, 13.56), 4.33 (dd, J=1.42, 5.58 Hz, 1H), 4.25 (m, 2H), 4.05 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.7 (J_{CP}=12.7 Hz), 97.5 (J_{CP}=9.4 Hz), 64.0 (J_{CP}=8.7 Hz). HRMS (matrix, NBA): calcd. for $C_4H_7O_3P•H^+$ 135.0133, found 135.0211.

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