Notes

A Facile Synthesis of α-Methyl(or phenyl)thiovinylphosponates

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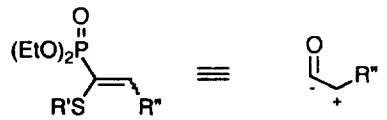
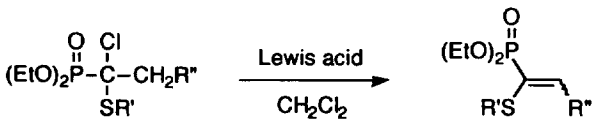
Vinylphosphonates (**2**) which are substituted with sulfenyl group at the α-position have been used as useful synthetic reagents for the preparations of heterocyclic or carbocyclic rings by Michael addition followed by intramolecular Horner-Wadsworth-Emmons (HWE) olefination.[1] It should be noted that the α-sulfenyl substituted vinylphosphonates (**2**) represent a masked synthon shown below in terms of the umpolung concept and the Michael addition products contain the α-phosphoryl sulfide functional group, which may be regarded as an acyl anion synthon.



So far, the numerous synthetic routes to the α-sulfenyl substituted vinylphosphonates (**2**) have been reported as follows; addition of elemental selenium to phosphonate carbanions followed by alkylation and oxidative elimination of the organoselenium group,[2] addition of methylsulfenyl chloride to vinylphosphonate followed by dehydrochlorination with base,[3] acid catalized dehydration of β-hydroxyphosphonates,[4] eliminative deoxygenation of α-phosphoryl sulfoxides,[5] and Peterson olefination of α-trimethylsilylphosponates.[1]

Bakuzis has briefly examined the preparation of vinyl sulfides from the chlorosulfides not activated by electron-withdrawing groups with pyridine. Thus ethyl phenyl sulfide on successive treatment with N-chlorosuccinimde (NCS) and refluxing in pyridine is converted into phenyl vinyl sulfide in 57% isolated yields.[6] The presence of electron-withdrawing groups (-COR, -COOR, -CN) α or β to the chloro sulfide function contributes significantly to the ease of HCl elimination with triethylamine[6] or pyrolysis.[7] Examination of literatures revealed that these reactions have not been used in the presence of α-phosphoryl group. Therefore, chloromethylphonates (**1**) were tested for the synthesis of vinyl phosphonates (**2**).



1 **2**

Table 1. Preparation of Diethyl 1-Methyl (or phenyl)thio-1-alkenylphosphonates (**2a-e**)

	Substituents (1) R′	R″	Lewis acid	Reaction time (h)	Yield[a] (%)	^{31}P NMR[b] ($CDCl_3/H_3PO_4$)
a	CH_3	H	$ZnBr_2$	18	70	16.03
			$TiCl_4$	18	72	
b	CH_3	CH_3[c]	$ZnBr_2$	8	85	16.67
			$TiCl_4$	8	88	
			$SnCl_4$	8	88	
c	CH_3	Ph[c]	$TiCl_4$	8	90	17.26
d	Ph	H	$TiCl_4$	18	73	23.77
e	Ph	CH_3[c]	$TiCl_4$	8	90	24.37
			$SnCl_4$	8	90	

[a] After isolation by column chromatography. [b] The conversion of positive ^{31}P NMR signals to low filed from H_3PO_4 is used. [c] Z/E isomeric ratios were not determined.

Treatment of chloromethylphosphonates (**1**) with Lewis acid offered the desired vinylphosphonates under mild conditions in good yields (Table 1). Lewis acids examined were zinc bromide, stannic chloride, and titanium(IV) chloride. E/Z isomeric ratios of the products (**2b**, **2c**, and **2e**) were not determined. This reaction presumably leads to the formation of sulfonium salt intermediate and the subsequent abstraction of β-proton by the counter ion.

Methyl (or phenyl)thiomethylphonates were prepared as described by Green[8] and were converted to the desired α-chlorosulfides (**1**) by alkylation[9] followed by chlorination[10] with N-chlorosuccinimide.

In conclusion, the reaction described here represents a convenient and novel method for preparing vinylphosphonates (**2**) from the readily available starting materials. Michael addition reactions to the products and its synthetic applications are in progress.

Experimental

General. ^{1}H NMR spectra were recorded on a Varian T-60A and FT-80A spectrometer using TMS as an internal standard (in $CDCl_3$). Multiplicity was simplified as follows: s=singlet, d=doublet, dd=doublet doublet, t=triplet, dq=double quatet, and m=multiplet. Infrared spectra were measured on a Perkin-Elmer 283B (in neat). ^{31}P NMR spectra were obtained on a Varian FT-80A spectrometer at 29.95 MHz. Chemical shifts were related to 85% H_3PO_4 as an external standard. Mass spectra were determined with a Hewlett-Packard 5985A through electron impack ionization method. Carbon tetrachloride and methylene chloride were refluxed and distillated from anhydrous calcium chloride and phosphorus pentoxide respectively. Tetrahydrofuran (THF) was distilled immediately prior to use from sodium/benzophe-

none. Column chromatography was performed using Kieselgel 60 (EM Science, 230-400 mesh) as stationary phase. Triethyl phosphite, chloromethyl methyl sulfide, chloromethyl phenyl sulfide, *n*-BuLi, N-chlorosuccinimide (NCS), and alkyl halides were obtained from commercial supplier, Aldrich and used without further purifications.

Alkylation of Diethyl methyl (or phenyl)thiomethylphosphonate. To a solution of diethyl methyl (or phenyl) thiomethylphosphonate (2.0 mmol)[8] in THF (10 mL) was added n-butyl lithium in hexane (2.2 mmol) at −78 ℃. The reaction mixture was stirred for 10-20 min. and then alkyl halides (2.0 mmol) (methyl iodide, ethyl bromide, and benzyl bromide) was added, warmed gradually to room temperature, allowed to stand for 2 h, neutralized, and extracted into chloroform. The organic phase was dried, filtered, and evaporated. The crude product was purified by distillation (75-85% yields). Product is identical with an authentic sample.[9]

Chlorination of α-Sulfenyl Phosphonates with NCS. To a suspension solution of N-chlorosuccinimide (6.2 mmol) in carbon tetrachloride (15 mL) was added diethyl methyl (or phenyl)thioalkylphosphonates (6.0 mmol) in carbon tetrachloride (50 mL) at room temperature. The reaction mixture was stirred for 4 h, filtered to remove succinimide, diluted with chloroform (10 mL) and hexane (10 mL), chilled, filtered off, and evaporated to give the crude products (**1**). The products were used without further purification.[10]

General Procedure for the Formation of Vinylphosphonates (2). To a solution of α-chloro alkylphosphonates (**1**) (5.0 mmol) in methylene chloride (25 mL) was added Lewis acid (5.0 mmol) at room temperature. The mixture was stirred for 8-18 h, quenched with water (5 mL), and separated. The organic phase was dried, filtered, and evaporated to a pale yellow liquid. The crude product was purified by column chromatography with diethyl ether as an eluent. Products (**2a, 2b** and **2c**) are identical with authentic samples.[1]

Diethyl 1-methylthio-1-ethenylphosphonate (2a). ^{1}H NMR δ 1.30 (t, 6H), 2.40 (s, 3H), 4.30 (dq, 4H), 5.60 (d, 1H, J=45), 6.12 (d, 1H, J=25); ^{31}P NMR δ 16.03; IR 1260 (P=O, s), 1060-1025 (P-O-C, vs); Mass (m/e, %) 109 (100), 149 (78), 155 (64), 210 (M^+, 48).

Diethyl 1-methylthio-1-propenylphosphonate (2b). ^{1}H NMR δ 1.30 (t, 6H), 2.12 (dd, 3H), 2.40 (s, 3H), 4.30 (dq, 4H), 7.12 (m, 1H); ^{31}P NMR δ 16.67; IR 1250 (P=O, s), 1050-1030 (P-O-C, vs); Mass (m/e, %) 71 (72), 135 (100), 153 (84), 191 (75), 224 (M^+, 73).

Diethyl 1-methylthio-1-styrenylphosphonate (2c). ^{1}H NMR δ 1.30 (t, 6H), 2.20 (s, 3H), 4.12 (dq, 4H), 7.16-8.00 (m, 6H); ^{31}P NMR δ 17.26; IR 1250 (P=O, s), 1060-1020 (P-O-C, vs).

Diethyl 1-phenylthio-1-ethenylphosphonate (2d). ^{1}H NMR δ 1.35 (t, 6H), 4.20 (dq, 4H), 5.85 (d, 1H, J=53), 6.12 (d, 1H, J=32), 7.30 (m, 5H); ^{31}P NMR δ 23.77; IR 1250 (P=O, s), 1050-1010 (P-O-C, vs).

Diethyl 1-phenylthio-1-propenylphosphonate (2e). ^{1}H NMR δ 1.35 (t, 6H), 2.10 (dd, 3H), 4.30 (dq, 4H), 7.20 (m, 5H), 7.40 (m, 1H); ^{31}P NMR δ 24.37; IR 1250 (P=O, s), 1060-1020 (P-O-C, vs); Mass (m/e, %) 115 (60), 134 (26), 147 (81), 286 (M^+, 100).

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Determination of Trace Impurities in ULSI Grade Silane

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Many electronic specialty gases (ESG's) have been used in the process manufacturing semiconductor devices. In the dry processes of ultra-large scale integrated (ULSI) fabrication, ESG's such as SiH_4, AsH_3, PH_3, B_2H_6 and etc are empolyed as dopant and/or epitaxial gases.[1]

Trace impurities in ESG's should be reduced as low as possible because they introduce defects in semiconductor devices[2,3]. The rapid development of semiconductor industries has made the measurement of the purity of ESG's vitally important. Therefore, it is indispensable to accurately measure trace impurities in ESG's in order to improve the yield.

Recently, world-famous gas companies have established relatively well analytical techniques for ESG's[4]. However, they have been reluctant to distribute the technologies. Unfortunately, even though the demand of ESG's continues to increase in Korea, semiconductor manufacturers have been using these gases without any analysis, because the analytical techniques for ESG's have not been available. Accordingly, there are many problems not only in the quality certification

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