3. Kim, D.; Economy, J. *Chem. Mater.* **1994**, *6*, 395.
4. Honstedt, L. F.; Schaeffer, G. W. *Advan. Chem. Ser.* **1961**, *32*, 232.
5. (a) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 6084. (b) Shore. S. G.; B ddeker, K. W. *Inorg. Chem.* **1964**, *3*, 914.
6. Sneddon, L. G.; Wideman, T. *Inorg. Chem.* **1995**, *34*, 1002.
7. Kim D.; Cofer, C. G.; Economy, J. *J. Am. Ceram. Soc.* **1995**, *78*(6), 1546.
8. Komm, R.; Geanangel, R. A.; Liepins, R. *Inorg. Chem.* **1983**, *22*, 1684.
9. Kwon, C. T.; McGee, H. A. Jr. *Inorg. Chem.* **1970**, *9*, 2458.
10. Fazen. P. J.; Beck, J. S.; Lynch, A. T.; Remsen, E. E.; Sneddon, L. G. *Chem. Mater.* **1990**, *2*, 96.
11. Gaines D. F.; Borlin, J. In *Boron Hydride Chemistry*; Muetteries, E. L., Eds.; Academic Press: New York, 1975; Chap 7.
12. Rice, R. W. *Am. Ceram. Soc. Bull.* **1983**, *62*(8), 889.
13. (a) Paciorek, K. J. L.; Harris, D. A.; Kratzer, R. H. *J. Polym. Sci., Polym. Chem.* **1986**, *24*, 173. (b) Bender, B. A.; Rice, R; Spann, J. R. *J. Am. Ceram. Soc.* **1987**, *70*, C-58.
14. Cofer, C. G. Ph. D. Thesis, 1996, 67.

Reaction of Phosphite with Acetal Derivatives: Syntheses of 1-Alkoxymethylphosphonates and 1-Alkylthiomethylphosphonates

Dae Young Kim*, Dong Il Han†, and Dong Young Oh‡

Department of Chemistry, Soonchunhyang University, Asan P.O. Box 97, Chungnam 336-600, Korea
†Taedok Institute of Technology, SK Corporation, Taejon 350-370, Korea
‡Department of Chemistry, Korea Advanced Institute of Science of Technology, Taejon 305-701, Korea
Recrived October 20, 1997

1-Alkoxymethylphosphonates **4** and 1-alkylthiomethylphosphonates **5** can be prepared by the reaction of acetal derivatives and diethyl trimethylsilyl phosphite in the presence of Lewis acid under mild conditions. The dependency of the chemoselectivities with Lewis acid on the reaction of O,S-acetals with phosphites is described.

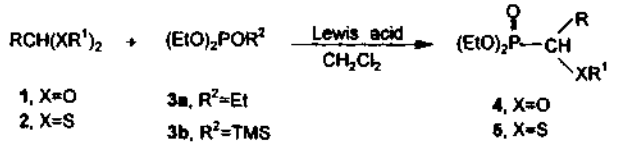
Introduction

Phosphonates are valuable intermediates for the formation of carbon-carbon double bonds because their use provides control of alkene regio- and stereoselectivity.[1] The α-substituted phosphonates are useful reagents in organic synthesis since they react easily with carbonyl compounds to form corresponding alkenes via the Horner-Wadsworth-Emmons (HWE) condensation.[1,2] 1-Alkoxymethylphosphonates and 1-alkyl(or aryl)mercaptomethylphosphonates are important intermediates for the conversion under HWE condition into α,β-unsaturated ethers and α,β-unsaturated sulfides, respectively, which afford the ketones by the subsequent hydrolysis. A number of synthetic approaches for the preparation of 1-alkoxymethylphosphonates and 1-alkyl (or aryl)mercaptomethylphosphonates have been developed, ranging from the direct Arbuzov reaction of trialkyl phosphites with α-haloalkyl ethers (or sulfides)[3] to the more sophisticated methods *via* [3,2] sigmatropic shift of S-allyl sulfides.[4] They have limitations in terms of the reaction conditions employed. The preparation of 1-alkoxy-1-arylmethylphosphonates have been reported by the reaction of benzaldehyde diethyl acetals with triethyl phosphite.[5] 1-Alkylthiomethylphosphonates have been obtained by the addition of dialkyl disulfide or elemental sulfur to alkylphosphonate carbanions,[6] alkylation of 1-mercaptoalkylphosphonates,[2c] and Friedel-Crafts reaction of chloro(alkylthio) methylphosphonate.[7]

In the course of our studies of α-substituted phosphonates,[8] we have developed the synthetic method for the preparation of 1-alkoxy (or 1-alkylmercapto)methylphosphonates from the reaction of diethyl trimethylsilyl phosphite with acetal derivatives.[9] Herein we report the reaction of phosphites with acetal derivatives in more details, providing information on its scopes and limitations.

Results and Discussion

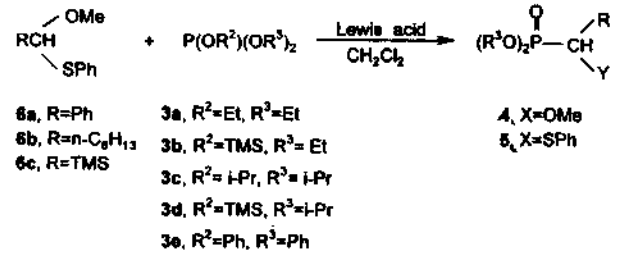
Synthesis of 1-Alkoxymethylphosphonates 4 and 1-Alkylmercaptomethyl-phosphonates 5. Diethyl trimethylsilyl phosphite **3b** has been widely used for various transformations and syntheses of both phosphorus and non-phosphorus containing compounds.[10] The presence of a silyl ester linkage rather than an alkyl ester in the phosphite increases the nucleophilicity of the phosphorus center and thus its reactivity in the Arbuzov type reactions.[11] Diethyl trimethylsilyl phosphite **3b** reacted with acetals **1** in the presence of Lewis acid to yield the 1-alkoxyalkylphosphonates **4** in good yields (Table 1). Treatment of acetals **1** with the Lewis acid presumably leads to formation of intermediate benzyl oxonium ions.[12] In a subsequent nucleophilic reaction diethyl trimethylsilyl phosphite **3b** reacts with this ions to yield products **4**.



Scheme 1.

The reaction proceeds satisfactorily with electron donating as well as electron withdrawing para-substituents on the aromatic moiety of **1** (Table 1, entries 7-12). This reaction required one equivalent of Lewis acid and the order of reactivity of Lewis acids was $SnCl_4$>$TiCl_4$>$BF_3\cdot OEt_2$>$ZnCl_2$ (Table 1, entries 2-5). It was found that diethyl trimethylsilyl phosphite **3b** was better nucleophile than triethyl phosphite **3a** (Table 1, entries 1, 2). Under same condition, diethyl trimethylsilyl phosphite **3b** reacted with arylaldehyde thioacetals **2** in the presence of stannic chloride to give desired 1-(substituted-aryl)alkylthiomethylphosphonates **5** in good yields (Table 1, entries 16-25). The advantages of this synthetic method for the preparation of 1-alkoxyl(or 1-alkylthio)alkylphosphonates are to give high yields and to be easy preparation of starting materials.

Reaction of O,S-Acetals 6 with phosphites 3 in the presence Lewis acids. In an extension of this work, we have found highly selective preparation of either 1-methoxyalkylphosphonates **4** or 1-phenylthioalkylphosphonates **5** from the reaction of O,S-acetals **6** with phosphites **3** in the presence of Lewis acid. As shown in Table 2, O,S-acetal **6a** shows the remarkable bias of the reaction products caused by alternation of the Lewis acid. Em-



Scheme 2.

ployment of $SnCl_4$ leads to **4** whereas **5** are produced by use of $TiCl_4$. The difference in reactivity of the Lewis acid may rationalize the unique switching effect. The high affinity of $TiCl_4$ towards oxygen[13] leaves the phenylthio group intact in this reaction. On the other hand, the predominant affinity of the tin atom to sulfur as well as the preferred stability of an intermediary α-methoxy carbocation governs the direction of the $SnCl_4$ promoted reaction. The chemoselectivity is highly dependent on the order of addition. The initial mixing of **6a** and **3a** followed by addition of Lewis acids, $SnCl_4$ and $TiCl_4$ led to the **4**:**5**=71:29 and **4**:**5**=60:40, respectively. Triphenyl phosphite **3e** shows the exclusive formation of **5**. The reaction of dialkyl trimethylsilyl phosphites (**3b** and **3d**) afforded the same reaction products as of trialkyl phosphites (**3a** and **3c**) though the yields are somewhat lower. However **6b** fails to give the remarkable selectivity in the carbon-phosphorus bond forming reaction. Regardless of Lewis acid employed, the product was obtained as a mixture of **4** and **5**. And **6c** also

Table 1. Synthesis of 1-alkoxyalkylphosphonates **4** and 1-alkylthioalkylphosphonates **5**

Entry	R	X	R^1	R^2	Lewis acid	Yield (%)	bp[a] (°C/mmHg)	^{31}P NMR[b]
1	Ph	O	Me	Et	$SnCl_4$	**4a**, 78	15-117/0.35	17.70
2	Ph	O	Me	TMS	$SnCl_4$	**4a**, 90		
3					$TiCl_4$	**4a**, 85		
4					$BF_3\cdot OEt$	**4a**, 81		
5					$ZnCl_2$	**4a**, 36		
6	Ph	O	Et	TMS	$SnCl_4$	**4b**, 92	116-119/0.35	19.62
7	*p*-OMe, C_6H_4	O	Me	TMS	$SnCl_4$	**4c**, 91	149-153/0.35	18.08
8	*p*-OMe, C_6H_4	O	Et	TMS	$SnCl_4$	**4d**, 95	122-124/0.35	17.20
9	*p*-Cl, C_6H_4	O	Me	TMS	$SnCl_4$	**4e**, 90	114-117/0.35	18.50
10	*p*-Cl, C_6H_4	O	Et	TMS	$SnCl_4$	**4f**, 88	116-119/0.35	18.72
11	*o*-Cl, C_6H_4	O	Et	TMS	$SnCl_4$	**4g**, 87	120-124/0.35	17.20
12	*p*-NO_2, C_6H_4	O	Et	TMS	$SnCl_4$	**4h**, 94	133-135/0.35	17.76
13	*p*-Me, C_6H_4	O	Et	TMS	$SnCl_4$	**4i**, 84	118-121/0.35	19.86
14	PhC≡C	O	Et	TMS	$SnCl_4$	**4j**, 75	119-124/0.30	18.10
15	*trans* PhCH=CH	O	Et	TMS	$SnCl_4$	**4k**, 88	125-128/0.30	18.53
16	2-thienyl	O	Et	TMS	$SnCl_4$	**4l**, 85	135-138/0.40	17.56
17	Ph	S	*n*-Bu	TMS	$SnCl_4$	**5a**, 80	125-128/0.35	22.2
18	Ph	S	Et	TMS	$SnCl_4$	**5b**, 75	110-113/0.40	22.2
19	*p*-Me, C_6H_4	S	*n*-Bu	TMS	$SnCl_4$	**5c**, 79	143-144/0.35	22.3
20	*p*-Me, C_6H_4	S	Et	TMS	$SnCl_4$	**5d**, 71	128-133/0.35	22.3
21	*p*-OMe, C_6H_4	S	*n*-Bu	TMS	$SnCl_4$	**5e**, 88	146-145/0.35	22.0
22	*p*-OMe, C_6H_4	S	Et	TMS	$SnCl_4$	**5f**, 81	144-145/0.35	21.8
23	*p*-Cl, C_6H_4	S	*n*-Bu	TMS	$SnCl_4$	**5g**, 72	136-140/0.35	22.7
24	*p*-Cl, C_6H_4	S	Et	TMS	$SnCl_4$	**5h**, 65	127-129/0.35	21.6
25	*p*-NO_2, C_6H_4	S	*n*-Bu	TMS	$SnCl_4$	**5i**, 68	140-150/0.30	20.5
26	*p*-NO_2, C_6H_4	S	Et	TMS	$SnCl_4$	**5j**, 60	140-143/0.35	20.1

[a]Kugelrohr distillation. [b]Positive chemical shifts are downfield from 85% H_3PO_4.

Table 2. Reaction of O,S-acetals **6** with phosphite **3**

Entry	O,S-Acetal, **6**	Phosphite, **3**	Lewis acid	Yield[a] (%)	Products (**4**:**5**)[b]
1	**6a**	3a	$SnCl_4$	73	100:0
2	**6a**	3a	$TiCl_4$	81	2:98
3	**6a**	3b	$SnCl_4$	61	96:4
4	**6a**	3b	$TiCl_4$	75	3:97
5	**6a**	3c	$SnCl_4$	80	98:2
6	**6a**	3c	$TiCl_4$	92	10:90
7	**6a**	3d	$SnCl_4$	72	100:0
8	**6a**	3d	$TiCl_4$	71	4:96
9	**6a**	3e	$SnCl_4$	90	5:95
10	**6a**	3e	$TiCl_4$	94	0:100
11	**6b**	3a	$SnCl_4$	77	60:40
12	**6b**	3a	$TiCl_4$	84	47:53
13	**6b**	3b	$SnCl_4$	57	89:11
14	**6b**	3b	$TiCl_4$	73	47:53
15	**6b**	3e	$TiCl_4$[c]	87	5:95
16	**6c**	3c	$TiCl_4$[c]	47	0:100

[a]Isolated yields by column chromatography. [b]Determined by Glc analysis. [c]The use of $SnCl_4$ afforded the same selectivity.

shows different results from **6a** and **6b**. In this case, only phenylthio(trimethylsilyl)methylphosphonate was isolated with both $SnCl_4$ and $TiCl_4$. The present process provides a highly selective preparation of α-heterosubstituted phosphonates.

In conclusion, the present synthetic route provides a convenient preparation of 1-alkoxyalkylphosphonates **4** and 1-alkylmercaptomethylphosphonates **5** from the reaction of acetals **1** and thioacetals **2** with diethyl trimethylsilyl phosphite **3b**. The reaction of O,S-acetals **6** with phosphites **3** affords chemoselectively **4** or **5** depending on Lewis acid employed.

Experimental

General

^{1}H NMR spectra were recorded on a Varian T-60A, FT-80A and Buruker AC 200 spectrometer using tetramethylsilane as an internal standard. ^{31}P NMR spectra obtained on a Varian FT-80A spectrometer at 29.95 MHz. Chemical shifts were related to 85% H_3PO_4 as an external standard. Chemical shifts are measured in part per million (δ) and coupling constants, J, are reported in Hz. Multiplicity was simplified such as s=singlet, bs=broad singlet, d=doublet, t=triplet, dq=double quatet, and m=multiplet. Infrared spectra were measured on a Perkin-Elmer 283B. Liquid and oils are performed in solution and intensities are designed such as s=strong and vs=very strong. Mass spectra were determined with a Hewlett-Packard 5985A through electron impact ionization method. Glc analyses were performed on a Hewlett Packard 5890A gas chromatograph using flame ionization detector and nitrogen gas as a carrier with Hewlett Packard 3390A integrator. Column used for analysis was SE-30. Methylene chloride was refluxed and distilled from phosphorus pentoxide. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Column chromatography was performed on Merck silica gel 60 (230-400 mesh). The acetals **1**[14], thioacetals **2**[14], O,S-acetals **6**[15], and diethyl trimethylsilyl phosphite **3b**[16] were prepared as reported previously.

General procedure of synthesis of 1-alkoxyalkylphosphonates 4 and 1-alkylthioalkylphosphonates 5. To a stirred solution of arylaldehyde dialkyl acetal derivatives **1** or **2** (2 mmol) in methylene chloride (10 mL) under nitrogen at 0 ℃ was slowly added stannic chloride (0.234 mL, 2 mmol). After 5 min of stirring at 0 ℃, diethyl trimethylsilyl phosphite **3b** (421 mg, 2 mmol) added into the reaction mixture. The resulting solution was left to return room temperature for 1-5 h. The reaction mixture was quenched by adding water (5 mL) and stirring 5 min. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated to leave pale yellow or colorless oil. The crude product was purified by Kugelrohr distillation or column chromatography with diethyl ether as an eluent.

General procedure for the Lewis acid mediated reaction of O-methyl S-phenyl acetal 6 with phosphites 3. To a solution of O,S-acetal **6** (1 mmol) in dry methylene chloride (5 mL) cooled to −78 ℃ was added dropwise with stirring Lewis acid (1 mmol). After 10 min, phosphite (1 mmol) in methylene chloride (2 mL) was added and the mixture was allowed to warm to room temperature for 1-4 h. The reaction mixture was poured into a cold saturated aqueous sodium hydrogen carbonate (10 mL) and extracted with methylene chloride (10 mL×3). The combined organic extracts was washed with brine, and dried with $MgSO_4$. The solvent was removed to give the crude product, which was purified by column chromatography on silica gel using ether as an eluent.

1-Methoxy-1-phenylmethylphosphonate (4a). bp 115-117 ℃/0.35 mmHg (lit.[5] 138-140 ℃/0.8 mmHg); ^{1}H NMR ($CDCl_3$) 1.27 (6H, t, $POCH_2\underline{CH_3}$), 3.40 (3H, s, OCH_3), 4.05 (4H, dq, $PO\underline{CH_2}CH_3$), 4.70 (1H, d, PCH, J=15 Hz), 7.45 (5H, s, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1070-1020 (vs); Mass (m/e) 258 (M^+, 14.6%), 121 (100).

1-Ethoxy-1-phenylmethylphosphonate (4b). bp 116-119 0.35 mmHg (lit.[5] 130-135 ℃/0.6 mmHg); ^{1}H NMR ($CDCl_3$) 1.26 (9H, t, $POCH_2\underline{CH_3}$, $OCH_2\underline{CH_3}$), 3.60 (2H, q, $O\underline{CH_2}CH_3$), 4.10 (4H, dq, $PO\underline{CH_2}CH_3$), 4.90 (1H, d, PCH, J=15 Hz), 7.45 (5H, s, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1060-1020 (vs); Mass (m/e) 272 (M^+, 35.5%), 135 (100).

1-Methoxy-1-(*p*-methoxyphenyl)methylphosphonate (4c). bp 149-153 ℃/0.35 mmHg; ^{1}H NMR ($CDCl_3$) 1.23 (3H, t, $OCH_2\underline{CH_3}$), 1.27 (6H, t, $POCH_2\underline{CH_3}$), 3.40 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 4.15 (4H, dq, $PO\underline{CH_2}CH_3$), 4.55 (1H, d, PCH, J=15.5 Hz), 6.80-7.70 (4H, m, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1050-1010 (vs); Mass (m/e) 288 (M^+, 5.8%), 151 (100), 137, 135.

1-Ethoxy-1-(*p*-methoxyphenyl)methylphosphonate (4d). bp 122-124 ℃/0.35 mmHg; ^{1}H NMR($CDCl_3$) 1.21 (3H, t, $OCH_2\underline{CH_3}$), 1.26 (6H, t, $POCH_2\underline{CH_3}$), 3.54 (2H, q, $O\underline{CH_2}CH_3$) 3.80 (3H, s, OCH_3), 4.10 (4H, dq, $PO\underline{CH_2}CH_3$), 4.60 (1H, d, PCH, J=15.5), 6.80-7.60 (4H, m, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1055-1020 (vs); Mass (m/s) 302 (M^+, 14.5%) 165 (100), 137 (36.6), 135 (56.8).

1-Methoxy-1-(*p*-chlorophenyl)methylphosphonate (4e). bp 114-117 ℃/0.35 mmHg; ^{1}H NMR($CDCl_3$) 1.26 (6H, t, $POCH_2\underline{CH_3}$), 3.40 (3H, s, OCH_3), 4.40 (4H, m, $PO\underline{CH_2}CH_3$), 4.58 (1H, d, PCH, J=15.6 Hz), 7.40 (4H, s, ArH); IR($CHCl_3$) 1250 (P=O, s), 1050-1000(vs); Mass(m/e)

292 (M^+, 25.0%), 171 (35.8), 169 (100), 157 (56.3), 155 (34.7).

1-Ethoxy-1-(*p*-chlorophenyl)methylphosphonate (4f). bp 116-119 ℃/0.35 mmHg (lit.[5] 130-135 ℃/0.6 mmHg); ^{1}H NMR($CDCl_3$) 1.22 (3H, t, $OCH_2\underline{CH_3}$), 1.27 (6H, t, $POCH_2\underline{CH_3}$), 3.60 (2H, q, $O\underline{CH_2}CH_3$), 4.10 (4H, dq, $PO\underline{CH_2}CH_3$), 4.66 (1H, d, PCH, J=16 Hz), 7.20-7.55 (4H, m, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1050-1010 (vs); Mass (m/s) 306 (M^+, 5.9%), 171 (76.9), 169 (100), 138 (46.8).

1-Ethoxy-1-(*o*-chlorophenyl)methylphosphonate (4g). bp 120-124 ℃/0.35 mmHg; ^{1}H NMR($CDCl_3$) 1.22 (3H, t, $OCH_2\underline{CH_3}$), 1.27 (6H, t, $POCH_2\underline{CH_3}$), 3.60 (2H, q, $O\underline{CH_2}CH_3$), 4.15 (4H, dq, $PO\underline{CH_2}CH_3$), 4.70 (1H, d, PCH, J =16.5), 7.10-7.55 (4H, m, ArH); IR($CHCl_3$) 1250 (P=O, s), 1050-1000 (vs); Mass(m/e) 306 (M^+, 12.3%), 171 (45.6), 169 (100).

1-Ethoxy-1-(*p*-nitrophenyl)methylphosphonate (4h). bp 133-135 ℃/0.35 mmHg; ^{1}H NMR($CDCl_3$) 1.26 (9H, t, $POCH_2\underline{CH_3}$, $OCH_2\underline{CH_3}$), 3.65 (4H, q, $O\underline{CH_2}CH_3$), 4.15 (4H, dq, $PO\underline{CH_2}CH_3$), 4.75 (1H, d, PCH, J=16.5), 7.51-8.45 (4H, m, ArH); IR($CHCl_3$) 1250 (P=O, s), 1050-1000 (vs); Mass(m/s) 317 (M^+, 14.9%), 180 (100).

1-Ethoxy-1-(*p*-tolyl)methylphosphonate (4i). bp 118-121 ℃/0.35 mmHg; ^{1}H NMR($CDCl_3$) 1.23 (3H, t, $OCH_2\underline{CH_3}$), 1.27 (6H, t, $POCH_2\underline{CH_3}$), 2.35 (3H, s, CH_3), 3.58 (2H, q, $O\underline{CH_2}CH_3$), 3.85-4.45 (4H, m, $PO\underline{CH_2}CH_3$), 4.65 (1H, d, PCH, J=16 Hz), 7.10-7.55 (4H, m, ArH); IR ($CHCl_3$) 1250(P=O, s), 1050-1010(vs); Mass(m/e) 286 (M^+, 1.8%), 149 (100).

1-Ethoxy-3-phenyl-2-propylphosphonate (4j). ^{1}H NMR($CDCl_3$) 1.21 (3H, t, $OCH_2\underline{CH_3}$), 1.27 (6H, t, $POCH_2\underline{CH_3}$), 3.60(2H, q, $O\underline{CH_2}CH_3$), 4.12 (4H, dq, $PO\underline{CH_2}CH_3$), 4.75 (1H, d, PCH, J=16.5 Hz), 7.45 (5H, s, ArH); IR ($CHCl_3$) 1250, 1060, 1020.

1-Ethoxy-3-phenyl-2-propylphosphonate (4k). ^{1}H NMR($CDCl_3$) 1.20 (3H, t, $OCH_2\underline{CH_3}$), 1.26 (6H, t, $POCH_2\underline{CH_3}$), 3.61 (2H, q, $O\underline{CH_2}CH_3$), 4.13 (4H, dq, $POCH_2\underline{CH_3}$), 4.63 (1h, d, PCH, J=16.3 Hz), 7.41 (5H, s, ArH); IR ($CHCl_3$) 1245, 1050-1020.

1-Ethoxy-1-(2-thiofuryl)methylphosphonate (4l). ^{1}H NMR($CDCl_3$) 1.19 (3H, t, $OCH_2\underline{CH_3}$), 1.25 (6H, t, $POCH_2\underline{CH_3}$), 3.60 (2H, q, $O\underline{CH_2}CH_3$), 4.15 (4H, dq, $PO\underline{CH_2}CH_3$), 4.70 (1H, d, PCH, J=16.2 Hz), 7.0-7.6 (3H, m, ArH); IR ($CHCl_3$) 1245, 1050-1010.

Diisopropyl methoxy(phenyl)methylphosphonate (4m). ^{1}H NMR ($CDCl_3$) δ 1.00-1.40 (12H, m), 3.35 (3H, s), 4.35 (1H, d, J=12 Hz), 4.60 (2H, m), 7.10-7.48 (5H, m); IR (film) 2980, 1255 (P=O), 1100, 1000.

Diethyl (methoxy)heptylphosphonate (4n). ^{1}H NMR ($CDCl_3$) δ 0.71-1.95(19H, m), 3.31(1H, m), 3.52 (3H, s), 4.15 (4H, dq); IR (film) 2935, 1245 (P=O), 1035; Mass (m/z, rel. intens.%) 266 (M^+, 5.5), 129 (67.7), 97 (100), (80.3).

1-Phenyl-1-buthylthiomethylphosphonate (5a). bp 125-128 ℃/0.35 mmHg; ^{1}H NMR($CDCl_3$) 0.71-1.45 (13H, m, $POCH_2\underline{CH_3}$, $SCH_2\underline{CH_2CH_2CH_3}$), 2.54 (4H, t, SCH_3), 4.01 (4H, dq, $PO\underline{CH_2}CH_3$), 4.05 (1H, d, PCH, J= 21.5 Hz), 7.26 (5H, s, ArH); IR($CHCl_3$) 1250(P=O, s), 1045-1020(vs); Mass(m/e) 316 (M^+, 4.3%), 228 (51.1), 179 (70.5), 91 (100).

1-Phenyl-1-buthylthiomethylphosphonate (5b). bp 110-112 ℃/0.35 mmHg; ^{1}H NMR($CDCl_3$) 1.16 (3H, t, $SCH_2\underline{CH_3}$), 1.28 (6H, t, $POCH_2\underline{CH_3}$), 2.51 (2H, t, SCH_2), 4.05 (1H, d, PCH, J=21.2 Hz), 4.07 (4H, dq, $PO\underline{CH_2}CH_3$), 7.26 (5H, s, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1030-1010 (vs); Mass (m/e) 288 (M^+, 4.0%), 228 (16.5), 151 (100).

1-(*p*-Tolyl)-1-buthylthiomethylphosphonate (5c). bp 143-144 ℃/0.35 mmHg; ^{1}H NMR($CDCl_3$) 0.75-1.56 (13H, m, $POCH_2\underline{CH_3}$, $SCH_2\underline{CH_2CH_2CH_3}$), 2.30 (3H, s, CH_3), 2.52 (2H, t, SCH_2), 3.99 (1H, d, PCH, J=20.1 Hz), 4.04 (4H, dq, $PO\underline{CH_2}CH_3$), 7.00-7.55 (4H, m, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1045-1000 (vs); Mass (m/s) 330 (M^+, 0.9%), 242 (68.4), 193 (82.3), 105 (100).

1-(*p*-Tolyl)-1-ethylthiomethylphosphonate (5d). bp 128-133 ℃/0.35 mmHg; ^{1}H NMR ($CDCl_3$) 1.20 (3H, s, CH_3), 2.58 (2H, q, SCH_2), 4.10 (1H, d, PCH, J=22.0 Hz), 4.14 (4H, dq, $PO\underline{CH_2}CH_3$), 6.95-7.55 (4H, m, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1030-990 (vs); Mass (m/e) 302 (M^+, 1.6%), 242 (41.5), 165 (100).

1-(*p*-Methoxyphinyl)-1-buthylthiomethylphosphonate (5e). bp 146-158 ℃/0.35 mmHg; ^{1}H NMR ($CDCl_3$) 0.73-1.45 (13H, m, $POCH_2\underline{CH_3}$, $SCH_2\underline{CH_2CH_2CH_3}$), 2.54 (2H, t, SCH_2), 3.72 (3H, s, OCH_3), 4.04 (1H, d, PCH, J=20.4 Hz), 4.06 (4H, dq, $PO\underline{CH_2}CH_3$), 6.79-7.54 (4H, m, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1020 (vs); Mass (m/e) 346 (M^+, 12.3%), 258 (43.8), 209 (98.6), 121 (100).

1-(*p*-Methoxyphenyl)-1-ethylthiomethylphosphonate (5f). bp 144-145 ℃/0.35 mmHg; ^{1}H NMR ($CDCl_3$) 1.17 (3H, t, $SCH_2\underline{CH_3}$), 1.29 (6H, t, $POCH_2\underline{CH_3}$), 2.51 (2H, q, $S\underline{CH_2}CH_3$), 3.74 (4H, s, OCH_3), 4.04 (1H, d, J= 21.0 Hz), 4.06 (4H, dq, $PO\underline{CH_2}CH_3$), 6.67-7.47 (1H, m, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1020-990 (vs); Mass (m/e) 318 (M^+, 4.3%), 258 (20.6), 181 (100).

1-(*p*-Chlorophenyl)-1-buthylthiomethylphosphonate (5g). bp 136-140 ℃/0.35 mmHg; ^{1}H NMR ($CDCl_3$) 0.75-1.55 (13H, m, $POCH_2\underline{CH_3}$, $SCH_2\underline{CH_2CH_2CH_3}$), 2.53 (2H, t, SCH_2), 4.00 (1H, d, PCH, J=18.9 Hz), 4.07 (4H, dq, $PO\underline{CH_2}CH_3$), 7.41 (4H, s, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1060-1120 (vs); Mass (m/e) 350 (M^+, 0.6%), 262 (30.6), 157 (64.6), 155 (40.1), 125 (100).

1-(*p*-Chlorophenyl)-1-ethylthiomethylphosphonate (5h). bp 127-129 ℃/0.35 mmHg; ^{1}H NMR ($CDCl_3$) 1.00-1.50 (9H, m, $POCH_2\underline{CH_3}$, $SCH_2\underline{CH_3}$), 2.54 (2H, q, SCH_2), 4.14 (4H, dq, $PO\underline{CH_2}CH_3$), 4.74 (1H, d, PCH, J=21.8 Hz), 7.41 (4H, s, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1030-990 (vs); Mass (m/e) 322 (M^+, 1.5%), 262 (33.3), 199 (73.6), 185 (100).

1-(*p*-Nitrophenyl)-1-buthylmethylphosphonate (5i). bp 140-145 ℃/0.3 mmHg; ^{1}H NMR ($CDCl_3$) 0.80-1.60 (13H, m, $POCH_2\underline{CH_3}$, $SCH_2\underline{CH_2CH_2CH_3}$), 2.56 (2H, t, SCH_2), 4.10 (4H, dq, $PO\underline{CH_2}CH_3$), 4.13 (1H, d, PCH, J= 20.6), 7.46-8.36 (4H, m, ArH); IR ($CHCl_3$) 1250 (P=O, s), 1040-1010 (vs); Mass (m/e) 361 (M^+, 0.6%), 273 (940.5), 136 (100).

1-(*p*-Nitrophenyl)-1-ethylthiomethylphosphonate (5j). bp 140-143 ℃/0.35 mmHg; ^{1}H NMR ($CDCl_3$) 1.23 (3H, t, $SCH_2\underline{CH_3}$), 1.35 (6H, t, $POCH_2\underline{CH_3}$), 2.59 (2H, t, SCH_2), 3.84-4.39 (5H, m, $PO\underline{CH_2}CH_3$, PCH), 7.55-8.43 (4H, m, ArH); IR ($CHCl_3$) 1245 (P=O, s), 1030-1000 (vs); Mass (m/e) 333 (M^+, 0.9%), 273 (64.4), 217 (47.5), 196 (100).

Diethyl phenyl(phenylthio)methylphosphonate (5k). ^{1}H NMR ($CDCl_3$) δ 1.29 and 1.60 (6H, t, J=6 Hz),

4.10 (4H, dq), 4.71 (1H, d, *J*=17 Hz), 7.05-7.50 (10H, m); IR (film) 2980, 1580, 1250 (P=O), 1035; Mass (m/z) 336 (M^+, 24.4%), 199 (100), 91 (80.3).

Diisopropyl phenyl(phenylthio)methylphosphonate (5l). ^{1}H NMR ($CDCl_3$) δ 1.97 (2H, d, *J*=6 Hz), 1.27 (10H, m), 4.28 (1H, d, *J*=22 Hz), 4.64 (2H, m), 6.98-7.53 (10H, m); IR (film) 2990, 1250 (P=O), 1000.

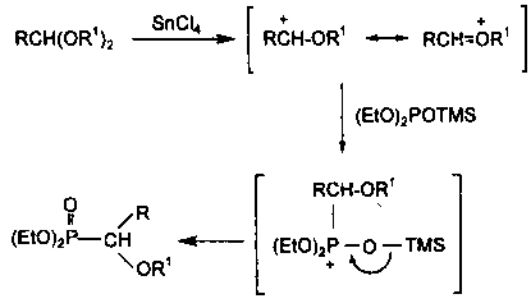
Diphenyl phenyl(phenylthio)methylphosphonate (5m). ^{1}H NMR ($CDCl_3$) δ 4.64 (1H, d, *J*=21 Hz), 6.74-7.67 (20H, m); IR (film) 2940, 1490, 1265 (P=O), 1215, 930; Mass (m/e) 432 (M^+, 37.9%), 199 (100), 165 (43.4).

Diethyl(phenylthio)heptylphosphonate (5n). ^{1}H NMR ($CDCl_3$) δ 0.54-2.08 (19H, m), 3.10 (1H, m), 4.16 (4H, dq), 7.10-7.63 (5H, m); IR (film) 2925, 1250 (P=O), 1040; Mass (m/e) 344 (M^+, 33.1%), 207 (60.3), 120 (100).

Diphenyl (phenylthio)heptylphosphonate (5o). ^{1}H NMR ($CDCl_3$) δ 0.65-2.28 (13H, m), 3.33 (1H, m), 6.93-7.67 (15H, m); IR (film) 2940, 1490, 1270 (P=O), 1190, 940.

Diethyl phenylthio(trimethylsilyl)methylphosphonate (5p). ^{1}H NMR ($CDCl_3$) δ 0.28 (9H, s), 1.23 (6H, t, *J*=5 Hz), 2.54 (1H, d, *J*=16 Hz), 4.02 (4H, dq), 7.08-7.50 (5H, m).

References

1. For general reviews, see: (a) Maryanoff, B. E.; Beitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (b) Wadsworth, W. S. Jr. *Org. React. (N.Y.)*, **1977**, *25*, 73. (c) Walker, B. J. *Organophosphorus Reagents in Organic Synthesis*, Cadogan, J. I. G., Ed.; Academic Press: New York, 1974, pp 155-206. (d) Kelly, S. E. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Schreiber, S. L., Eds.; Pergamon Press: Oxford, 1991; Vol. 1, Chapter 3. 1, pp 755-782.
2. (a) Mastalerz, P. *Handbook of Organophosphorus Chemistry*, Engel, R., Ed.; Marcel Dekker: New York, 1992, Chapter 7. (b) Corey, E. J.; Shulman, J. I. *J. Org. Chem.* **1970**, *35*, 777. (c) Mikolajczyk, M.; Grzejazczak, S.; Chefczynska, A.; Zaterski, A. *J. Org. Chem.* **1979**, *44*, 2967. (d) Kluge, A. F. *Tetrahedron Lett.* **1978**, *19*, 3629.
3. (a) Schaumann, E.; Grabky, F. F. *Liebigs Ann. Chem.* **1977**, *88*, 862. (b) Farrington, G. K.; Kumar, A.; Wedler, F. C. *Org. Proc. Prep. Int.* **1989**, *21*, 390. (c) Holy, A.; Rosenberg, I.; Dvorakova, H. *Coll. Czech. Chem. Commun.* **1989**, *54*, 2190.
4. Makomo, H.; Masson, S.; Saquet, M. *Tetrahedron Lett.* **1993**, *34*, 7257.
5. Burkhouse, D.; Zimmer, H. *Synthesis* **1984**, 330.
6. Mikolajczyk, M.; Balczewski, P.; Grzejszak, S. *Synthesis* **1980** 127.
7. Kim, T. H.; Oh, D. Y. *Tetrahedron Lett.* **1986**, *27*, 1165.
8. (a) Kim, T. H.; Kim, D. Y.; Oh, D. Y. *Synth. Commun.* **1987**, *17*, 953. (b) Kim, D. Y.; Oh, D. Y. *Bull Korean Chem. Soc.* **1986**, *16*, 859. (c) Kim, D. Y.; Lee, K.; Oh, D. Y. *J. Chem. Soc. Perkin Trans 1.* **1992**, 2451.
9. (a) Kim, D. Y.; Oh, D. Y. *Synth. Commun.* **1986**, *16*, 859. (b) Kim, D. Y.; Kim, T. H.; Oh, D. Y. *Phosphorus Sulfur* **1987**, *34*, 179. (c) Han, D. I.; Kim, D. Y.; Oh, D. Y. *Bull. Korean Chem. Soc.* **1989**, *10*, 329.
10. (a) Lopusinski, A.; Michalski, J.; Potrzebowski, M. *Phosphorus Sulfur* **1986**, *28*, 299. (b) Dembinski, R.; Koninski, R.; Michalski, J.; Skowronka, A. *J. Chem. Soc. Chem. Commun.* **1986**, 1770. (c) Michalski, J.; Lopusinski, A.; Jezierska, B.; Luczak, L.; Potrzebowski, M. *Phosphorus Sulfur* **1987**, *30*, 221. (d) Evans, D. A.; Hurst, K. M.; Takacs, J. M. *J. Am. Chem. Soc.* **1979**, *100*, 3467. (e) Sekine, M.; Nakajima, M.; Hata, T. *J. Org. Chem.* **1981**, *46*, 4030.
11. Wozniak, L.; Chojnowski, J. *Tetrahedron* **1989**, *45*, 2465.
12. 

13. Chemoselective allylation or propargylation with BF_3·OEt_2 and $TiCl_4$ has been observed in the reaction of O, S-acetals with allyl (or allenyl)tin compounds: Sato, T.; Okura, S.; Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1987**, *28*, 6299.
14. Ong, B. S.; Chan, T. H. *Synth. Commun.* **1977**, *7*, 283.
15. (a) Jensen, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 1476. (b) Mandai, T.; Hara, K.; Nakajima, J.; Kawada, M.; Otera, J. *Tetrahedron Lett.* **1983**, *24*, 4993.
16. (a) Sekine, M.; Okimota, K.; Yamada, K.; Hata, T. *J. Org. Chem.* **1981**, *46*, 1097. (b) Issleib, K.; Walter, B. *Angew Chem. Int. Ed. Engl.* **1967**, *6*, 8.