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Formation and Reactions of α-Phosphoryl Thiocarbocations: Synthesis of α-Sulfenyl Phosphonates

Taek Hyeon Kim* and Dong Young Oh†

Department of Fine Chemical Technology, Chonnam National University, Kwangju 500-757, Korea
†Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea
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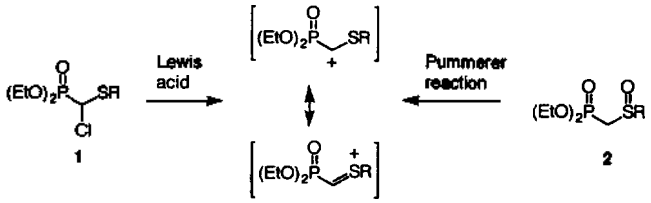
The reaction of chloro(methylthio and arylthio)methanephosphonate (1) and Pummerer-type reaction of sulfinylmethanephosphonate (2) with nucleophiles such as aromatic compounds and thiols were examined. The direct chlorination of (methylthio and arylthio)methanephosphonate with *N*-chlorosuccinimide (NCS) led to the formation of monochlorinated phosphonates (1) in good yield. The reaction of 1 with aromatic compounds and thiols in the presence of stannic chloride afforded a variety of aryl(methylthio)methanephosphonates (3) and thioacetals of formylphosphonates (4), respectively. Phosphonates 3 and 4 were also obtained from the reaction of Pummerer intermediate, generated from sulfinylmethanephosphonate (2), with aromatic compounds and thiols, respectively. A versatile reaction conditions to generate Pummerer intermediate were examined. The best condition was the combination of trifluoroacetic anhydride with stannic chloride. All reactions may involve an initial formation of α-phosphoryl thiocarbocation and a subsequent nucleophilic attack of aromatic compounds and thiols.

Introduction

Phosphonates are important reagents for the construction of carbon-carbon double bonds because their use provides control of olefin regio- and stereoselectivity.[1] Phosphonates containing organic sulfur group have emerged as the subject of considerable interest in organic synthesis.[2] In our preliminary report we described the reaction of chloro(methylthio and arylthio)methanephosphonate (1)[3] and Pummerer-type reaction of sulfinylmethanephosphonate (2)[4] with various nucleophiles to afford several α-sulfenyl substituted phosphonates. These reactions involve the generation of α-phosphoryl thiocarbocations as the corresponding intermediates from either the treatment of 1 with Lewis acid or Pummerer rearrangement of 2 (Scheme 1).

According to the previous report,[5] aryl(methylthio)methanephosphonates (3) was converted into aromatic ketones under the Horner-Wadsworth-Emmons reaction conditions followed by hydrolysis. The preparation of 3 results from the addition of the elemental sulfur[5] or disulfide[6] to arylmethanephosphonate cabanion and the reaction of thioacetal with phosphite[7] to overcome the synthetic limitation of aryl substituent in Arbusov reaction. Thioacetals of formylphosphonate (4) are the precursors of ketene thioacetals which

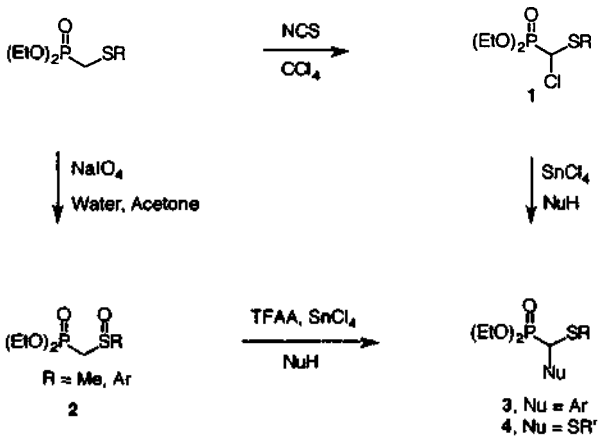


Scheme 1.

are reagents of great synthetic potential. So far a few reports on the synthesis of 4 have been found in the literature.[8] In this report the syntheses of aryl(methylthio)methanephosphonates and thioacetals of formylphosphonate will be described in detail (Scheme 2).

Results and Discussion

Synthesis of Aryl(methylthio)methanephosphonates. Chloro(methylthio and arylthio)methanephosphonates (1) were prepared from direct chlorination of methyl (and aryl)thiomethanephosphonate with *N*-chlorosuccinimide (NCS) and used for further reaction without purification (Table 1).[3a] Given the best yields by using a 10-20% excess



Scheme 2.

Table 1. Preparation of Chloro(R-thio)methanephosphonates (1)

Run	R	Yield (%)[a]	^{31}P NMR[b]
1a	CH_3	98	+14.1
1b	Ph	98	+14.3
1c	4-MePh	96	+13.6
1d	4-ClPh	94	+13.1

[a] Yield of the crude product. [b] The conversion of positive ^{31}P NMR signals to low field from H_3PO_4 is used.

Table 2. Reaction of Benzene with **1a**

Benzene/**1a**[a]	Lewis acid	Yield (%)[b]
5	$SnCl_4$	85
5	$TiCl_4$	82
5	$ZnCl_2$	23
1	$SnCl_4$	81
1	$TiCl_4$	78
1	$ZnCl_2$	18

[a] The mole fraction. [b] Isolated yield by column chromatography.

of NCS in arylthiomethanephosphonates, it was proved to give only monochlorinated phosphonate with no detectable amount of dichlorinated phosphonate by means of the careful examination of phosphorus NMR. Chloro(methylthio)methanephosphonate was prepared with treatment of one equivalent of NCS and purified by distillation (yield 85%, bp 118-120 ℃/1.6 mm).

As expected, α-phosphoryl-α-chloro sulfides were useful as reactive electrophiles for sulfur-mediated reactions. Lewis acid-catalyzed reaction with aromatic compounds in methylene chloride was employed to prepare aryl(methylthio) methanephosphonate. Reaction of **1** with benzene under a variety of conditions showed that (1) the reaction required one equvalent of Lewis acid and gave no polyalkylated product, and (2) the order of reactivity of Lewis acids was $SnCl_4$ >$TiCl_4$>$ZnCl_2$ (Table 2). Therefore, we performed the reaction of **1** with substituted benzenes in the presence of stannic chloride. In the case of toluene, cumene, isobutylbenzene,

Table 3. Preparation of Aryl(methylthio)methanephosphonates (3)

Run	ArH	Yield (%)[a] A[c]	B[d]	^{31}P NMR[b]
3a	Benzene	85	87	+22.1
3b	Toluene	91(1/3)	86(1/4)	+22.2
3c	Cumene	94(1/4)	95(1/5)	+22.3
3d	*i*-Bu-benzene	99(1/6)	94(1/7)	+22.4
3e	*t*-Bu-benzene	99(1/7)	99(1/8)	+22.4
3f	*p*-Xylene	90	88	+22.8
3g	Durene	78	75	+25.5
3h	*p*-Diethylbenzene	99	92	+22.8

[a] Parenthesis is the ratio of *ortho*- to *para*- isomers determined by GC. [b] The conversion of positive ^{31}P NMR signals to low field from H_3PO_4 is used. [c] Method A: by the Friedel-Crafts reaction. [d] Method B: by the Pummerer-type reaction.

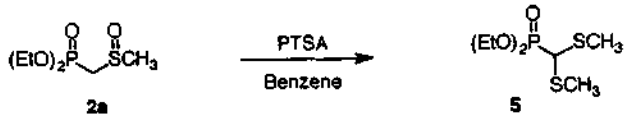
Table 4. Pummerer-Type reaction of **2a** with Benzene

Run	Activator of Sulfoxide	Reaction Temp.	Time (h)	Yield (%)[a]
1	TsOH (2 eq.)	Reflux	2.5	[b]
2	CF_3COOH (2 eq.)	Reflux	3.5	[b]
3	CF_3COOH (Sol.)	Reflux	3.5	65
4	$(CF_3CO)_2O$ (2 eq.)	Reflux	1.5	[c]
5	$(CF_3CO)_2O$-CF_3COOH	0-rt	1.0	73
6	$(CF_3CO)_2O$-$SnCl_4$	0	0.8	87
7	$(CH_3CO)_2O$-$SnCl_4$	rt	0.8	0
8	$(CF_3CO)_2O$-$BF_3(OEt)_2$	0-rt	0.8	40
		rt	2.0	80

[a] Isolated yield by column chromatography. [b] (Dimethylthio) methane phosphonate was obtained. [c] Trifluoroacetoxy-substituted phosphonate was obtained.

and *ter*-butylbezene, the mixture of *ortho*-and *para*- isomers was obtained and its ratio was determined by GC as shown in Table 3.[9] A reaction of chlorobezene with **1** failed at room temperature. Our synthetic method provides a very simple and convenient direct introduction of an aromatic group into the α-position of phosphonates *via* α-phosphoryl thiocarbocations.

Pummerer intermediate generated from α-sulfinyl methanephosphonate was also expected to be α-phosphoryl thiocarbocation. We examined the Pummerer-type reaction of methylsulfinyl methanephosphonate with benzene under a variety of conditions (Table 4). Reflux of **2a** with two equivalents of *p*-toluenesulfonic acid (PTSA) or trifluoroacetic acid (TFA) for 2 h gave diethyl dimethylthiomethane phosphonate (**5**) (Scheme 3). Reflux of **2a** with benzene (5 eq.) in an excess TFA(solvent) for 3 h resulted in the desired product. This suggests that the excess TFA holds the water formed during the reaction, preventing the formation of **5**.[10] The use of acetic anhydride other than acid is expected to be a more effective activator of sulfoxide. Treatment of **2a** with trifluoro acetic anhydride (TFAA) in boiling benzene for 2 h afforded only the undesired 1-trifluoroacetoxy phosphonate. However,



Scheme 3.

Table 5. Reaction of **1a** with 1-Propanethiol

Run	Lewis acid	Reaction time (h)	Yield (%)[a]
1	$SnCl_4$	1.0	74
2	$TiCl_4$	1.0	72
3	$ZnCl_2$	1.0	54
4	$ZnCl_2$	2.0	70

[a]Isolated yield by column chromatography.

Table 6. Preparation of Thioacetals of Formylphosphonate (**4**)

Run	R	R′	Yield (%)[a] A[c]	B[d]	^{31}P NMR[b]
4a	C_6H_5	$CH_3CH_2CH_2$	74	65	+21.37
4b	C_6H_5	$(CH_3)_2CH$	76	62	+21.33
4c	C_6H_5	$(CH_3)_2CHCH_2$	77	67	+20.93
4d	C_6H_5	C_6H_5	82	70	+21.23
4e	C_6H_5	$C_6H_5CH_2$	84	70	+21.80
4f	$4\text{-}CH_3C_6H_4$	$CH_3CH_2CH_2$	75		+21.78
4g	$4\text{-}CH_3C_6H_4$	$(CH_3)_2CH$	73		+21.58
4h	$4\text{-}CH_3C_6H_4$	C_6H_5	76		+21.27

[a]Isolated yield by column chromatography. [b]The conversion of positive ^{31}P NMR signals to low field from H_3PO_4 is used. [c]Method A: by the Friedel-Crafts reaction. [d]Method B: by the Pummerer-type reaction.

the desired product was obtained in 73% yield by treatment with the mixture of TFAA and TFA. TFAA/Lewis acid in methylene chloride was also tested. The use of acetic anhydride in place of TFAA showed no sign of reaction process at room temperature. The best conditions for the formation of aryl(methylthio)methanephosphonates was found to use the mixture of TFAA and $SnCl_4$ as activator at 0 ℃. As with Friedel-Crafts reaction, this synthetic method is also available to the aromatic compounds with electron-donating group. In the case of toluene, cumene, isobutylbenzene, and *ter*-butylbezene, the mixture of *ortho*-and *para*- isomers was obtained and its ratio was determined by GC as shown in Table 3.[11]

Synthesis of Thioacetals of Formylphosphonate. Thioacetals of formylphosphonate (**4**) are the derivatives of the practically unknown formyl phosphonate. The Lewis acid-catalyzed reaction of **1** with thiol led to the formation of the thioacetals of formyl phosphonate *via* thiocarbocation intermediate. The best yield was obtained from stannic chloride (Table 5). The product obtained was either colorless or pale yellow oils. They are shown in Table 6.

Compounds **4** were also easily obtained by performing the Pummerer-type reaction of sulfinyl methanephosphonate with thiols (Table 7). As in the case of aromatic compounds the best activator was the combination of TFAA and stannic chloride. Acetic anhydride/$SnCl_4$ failed and the combination of TFAA and boron trifluororide afforded 1-trifluoro acetoxy phosphonate at room temperature.

Table 7. Pummerer-Type Reaction of **2b** with 1-Propanethiol

Run	Activator of Sulfoxide	Reaction Temp.	Time (h)	Yield (%)[a]
1	$(CH_3CO)_2O\text{-}SnCl_4$	rt	2.0	[b]
2	$(CF_3CO)_2O\text{-}SnCl_4$	0-rt	0.8	65
3	$(CF_3CO)_2O\text{-}TiCl_4$	0-rt	0.8	62
4	$(CF_3CO)_2O\text{-}BF_3(OEt)_2$	0-rt	1.0	[c]

[a]Isolated yield by column chromatography. [b]No reaction occurred. [c]Trifluoroacetoxy-substituted phosphonate was obtained.

All reactions may involve the initial formation of α-phosphoryl thiocarbocation and a subsequent nucleophilic attack of aromatic compounds and thiols. In conclusion these reactions described here represent a convenient and novel method for the preparation of α-sulfur substituted phosphonates.

Experimental

General. ^1H NMR spectra were recorded on a Varian T-60A and FT-80A spectrometer using tetramethylsilane as an internal standard. Chemical shifts are measured in parts per million (δ) and coupling constants, *J*, are reported in hertz. 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. ^{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 impact ionization method. Methylene chloride and carbon tetrachloride were refluxed and distilled from phosphorus pentoxide. Column chromatography was performed using Kieselgel 60 (EM Science, 230-400 mesh) as a stationary phase.

Chlorination of Sulfenyl Phosphonates with NCS. To a suspension of N-chlorosuccinimide (0.018 g, 6.0 mmol) in carbon tetrachloride (17 mL) was added diethyl methyl (and aryl)thiomethanephosphonate (5.0 mmol)[12] in carbon tetrachloride (3 mL). The reaction mixture was stirred for 3 h at room temperature under nitrogen atmosphere. Then the insoluble materials were removed by filteration and the filtrate was concentrated, diluted with a solution of chloroform (4 mL) and hexane (4 mL), chilled, filtered, and evaporated to give the crude product.

Diethyl chloro(methylthio)methanephosphonate (1a). ^1H NMR ($CDCl_3$) δ 1.48 (6H, t), 2.52 (3H, s), 4.38 (4H, dq), 5.08 (1H, d, *J*=12 Hz); IR ($CHCl_3$) 3010, 1260 (P=O, s), 1060-1025 (vs) cm^{-1}.

Diethyl chloro(phenylthio)methanephosphonate (1b). ^1H NMR ($CDCl_3$) δ 1.52 (6H, t), 4.43 (4H, dq), 5.40 (1H,

d, J=12 Hz), 7.40-7.83 (5H, m); IR ($CHCl_3$) 1260 (P=O, s), 1059-1020 (vs) cm^{-1}.

Diethyl chloro(4-methylphenylthio)methanephosphonate (1c). recrystalized from hexane. mp 34-36 ℃. ^1H NMR ($CDCl_3$) δ 1.37 (6H, t), 2.33 (3H, s), 4.23 (4H, dq), 5.25 (1H, d, J=13 Hz), 7.06-7.53 (4H, m); IR ($CHCl_3$) 1265 (P=O, s), 1050-1020 (vs) cm^{-1}.

Diethyl chloro(4-chlorophenylthio)methanephosphonate (1d). recrystalized from hexane. mp 36-37 ℃. ^1H NMR ($CDCl_3$) δ 1.40 (6H, t), 4.25 (4H, dq), 5.39 (1H, d, J=14 Hz), 7.20-7.67 (4H, m); IR ($CHCl_3$) 1260 (P=O, s), 1250-1020 (vs) cm^{-1}.

Synthesis of Aryl(methylthio)methanephosphonate. Method A: by the Friedel-Crafts reaction. To a stirred solution of diethyl chloro (methylthio)methanephosphonate (0.33 g, 1.4 mmol) and aromatic compound (1.4 mmol) in methylene chloride (5 mL) in an ice bath was added stannic chloride (0.26 mL, 1.4 mmol) dropwise. The reaction mixture was stirred at room temperature for 40 min, quenched with water, extracted with chloroform, dried, filtered, and evaporated. The crude product was chromatographed on silica gel using ether.

Method B: by the Pummerer rearrangement intermediate. To a stirred solution of methylsulfinyl methanephosphonate (0.26 g, 1.2 mmol)[13] and aromatic compound (1.2 mmol) in methylene chloride (5 mL) under nitrogen atmosphere in an ice bath was slowly added trifluoroacetic anhydride (1.2 mmol). In 10 min stannic chloride (1.2 mmol) was added dropwise. The reaction mixture was stirred in an ice bath for 40 min, quenched with water (5 mL), and extracted with chloroform. The organic layer was washed with diluted sodium hydrogen carbonate, dried, filtered, and evaporated. The crude product was purified by column chromatography.

Diethyl phenyl(methylthio)methanephosphonate (3a). ^1H NMR ($CDCl_3$) δ 1.18 and 1.33 (6H, t), 2.11 (3H, s), 3.78 (1H, d, J=20 Hz), 4.03 (4H, dq), 7.21-7.52 (5H, m); IR ($CHCl_3$) 1265 (P=O, s), 1060-1030 (vs) cm^{-1}.

Diethyl 2-and 4-methylphenyl(methylthio)methanephosphonate (3b). ^1H NMR ($CDCl_3$) δ 1.14 and 1.30 (6H, t), 2.07 (3H, s), 2.35 (3H, s), 3.80 (1H, d), 3.97 (4H, dq), 6.69-7.40 (4H, m); IR ($CHCl_3$) 1265 (P=O, s), 1050-1030 (vs) cm^{-1}; Mass (m/e, %) 151 (100.0), 242 (38.5), 288 (M, 1.9).

Diethyl 2-and 4-isopropylphenyl(methylthio)methanephosphonate (3c). ^1H NMR ($CDCl_3$) δ 1.15 and 1.33 (6H, t), 1.30 (6H, d), 2.12 (3H, s), 2.85-2.90 (1H, m), 3.90 (1H, d), 4.03 (4H, dq), 7.10-7.48 (4H, m); IR ($CHCl_3$) 1250 (P=O, s), 1060-1025 (vs) cm^{-1}.

Diethyl 2- and 4-isobutylphenyl(methylthio)methanephosphonate (3d). ^1H NMR ($CDCl_3$) δ 0.95 (6H, d), 1.16 and 1.30 (6H, t), 1.60-1.75 (1H, m), 2.12 (3H, s), 2.51 (2H, d), 3.78 (1H, d, J=20 Hz), 4.02 (4H, dq). 7.00-7.43 (4H, m); IR ($CHCl_3$) 1265 (P=O, s), 1060-1035 (vs) cm^{-1}.

Diethyl 2- and 4-*t*-butylphenyl(methylthio)methanephosphonate (3e). ^1H NMR ($CDCl_3$) δ 1.13 and 1.30 (6H, t), 1.35 (9H, s), 2.10 (3H, s), 3.93 (1H, d, J=20 Hz), 4.05 (4H, dq), 7.36 (4H, bs); IR ($CHCl_3$) 1265 (P=O, s), 1060-1030 (vs) cm^{-1}; Mass (m/e, %) 193 (100.0), 284 (59.6), 330 (M, 1.9).

Diethyl 2,5-dimethylphenyl(methylthio)methanephosphonate (3f). ^1H NMR ($CDCl_3$) δ 1.17 and 1.37 (6H, t), 2.12 (3H, s), 2.37 (6H, s), 3.98 (1H, d), 4.03 (4H, dq), 6.97 (2H, s), 7.43 (1H, s); IR ($CHCl_3$) 1260 (P=O, s), 1060-1030 (vs) cm^{-1}.

Diethyl 2,3,5,6-tetramethylphenyl(methylthio)methanephosphonate (3g). ^1H NMR ($CDCl_3$) δ 1.03 and 1.37 (6H, t), 2.23-2.38 (15H, m), 3.58-4.59 (5H, m), 6.87 (1H, s); IR ($CHCl_3$) 1265 (P=O, s), 1060-1030 (vs) cm^{-1}.

Diethyl 2,5-diethylphenyl(methylthio)methanephosphonate (3h). ^1H NMR ($CDCl_3$) δ 0.97-1.47 (12H, m), 2.13 (3H, s), 2.67 (4H, q), 4.03 (1H, d), 4.08 (4H, dq), 7.00 (2H, s), 7.47 (1H, s); IR ($CHCl_3$) 1265 (P=O, s), 1060-1035 (vs) cm^{-1}.

Diethyl dimethylthiomethanephosphonate (5). Methylsulfinylmethanephosphonate (0.28 g, 1.3 mmol) was refluxed for 2 h with *p*-toluenesulfonic acid or trifluoroacetic acid (2.6 mmol) in benzene (5 mL). The reaction mixture was washed with a saturated sodium hydrogen carbonate solution, dried, and evaporated. ^1H NMR ($CDCl_3$) δ 1.45 (6H, t), 2.31 (6H, s), 3.61 (1H, d), 4.21 (4H, dq).

Synthesis of Thioacetals of Formylphosphonate. Method A: by Friedel-Crafts Reaction. To a stirred solution of diethyl chloro(phenylthio)methanephosphonate (1.4 mmol) in methylene chloride (5 mL) at 0 ℃ was slowly added stannic chloride (0.26 mL, 1.4 mmol). In 5 min thiol (1.4 mmol) was added to the reaction mixture. The resulting solution was warmed to room temperature and stirred for 40 min, quenched with saturated sodium hydrogen carbonate (10 mL), extracted with chloroform (5 mL×3), dried, and evaporated. The crude product was purified by column chromatography using ethyl acetate.

Method B: by the Pummerer rearrangement intermediate. Trifluoroacetic anhydride (1.2 mmol) was added to a solution of phenylsulfinylmethanephosphonate (0.32 g, 1.2 mmol) in methylene chloride (4 mL) under nitrogen atmosphere in an ice bath. After successive addtion of stannic chloride and thiol, the reaction mixture was stirred for 0.8 h, quenched with water, extracted with chloroform, dried, and evaporated.

Diethyl phenylthio(*n*-propylthio)methanephosphonate (4a). ^1H NMR ($CDCl_3$) δ 0.97 (3H, t), 1.37 (6H, t), 1.67 (2H, m), 2.83 (2H, t), 4.05 (1H, d), 4.18 (4H, dq), 7.25-7.67 (5H, m); IR ($CHCl_3$) 3075, 2998 (s), 1260 (P=O, s), 1050-1035 (vs), 965 cm^{-1}; Mass (m/e, %) 89 (100), 127 (47.3), 169 (40.9), 225 (65.4), 260 (79.0), 334 (M, 5.8).

Diethyl isopropylthio(phenylthio)methanephosphonate (4b). ^1H NMR ($CDCl_3$) δ 1.30 (6H, d), 1.33 (6H, t), 3.37 (1H, m), 4.13 (1H, d), 4.17 (4H, dq), 7.23-7.50 (5H, m); IR ($CHCl_3$) 3080, 3000, 1265 (P=O, s), 1055-1030 (vs), 970 cm^{-1}; Mass (m/e, %) 127 (66.4), 155 (74.5), 183 (100), 225 (49.3), 260 (42.2), 334 (M, 2.3).

Diethyl isobutylthio(phenylthio)methanephosphonate (4c). ^1H NMR ($CDCl_3$) δ 0.93 (6H, d), 1.30 (6H, t), 1.67 (1H, m), 2.70 (2H, d), 4.10 (1H, d), 4.25 (4H, dq), 7.17-7.67 (5H, m); IR ($CHCl_3$) 3070, 2975, 1269 (P=O, s), 1055-1030 (vs), 965 cm^{-1}.

Diethyl bisphenylthiomethanephosphonate (4d). ^1H NMR ($CDCl_3$) δ 1.27 (6H, t), 4.13 (4H, dq), 4.40 (1H, d), 7.10-7.50 (10H, m); IR ($CHCl_3$) 3070, 3000, 1260 (P=O, s), 1050-1025 (vs), 970 cm^{-1}.

Diethyl benzylthio(phenylthio)methanephosphonate (4e). ^1H NMR ($CDCl_3$) δ 1.28 (6H, t), 3.93 (1H, d), 3.97 (2H, s), 4.20 (4H, dq), 7.22 (10H, bs); IR ($CHCl_3$) 3070,

2990, 1260 (P=O, s), 1050-1025 (vs), 965 cm^{-1}; Mass (m/e, %) 91 (100), 260 (53.3), 382 (M, 0.52).

Diethyl 4-methylphenylthio(n-propylthio)methanephosphonate (4f). ^1H NMR ($CDCl_3$) δ 0.92 (3H, t), 1.28 (6H, t), 1.58 (2H, m), 2.28 (3H, s), 2.80 (2H, t), 3.95 (1H, d), 4.13 (4H, dq), 7.00-7.50 (4H, m); IR ($CHCl_3$) 1260 (P=O, s), 1055-1030 (vs) cm^{-1}.

Diethyl isopropylthio(4-methylphenylthio)methanephosphonate (4g). ^1H NMR ($CDCl_3$) δ 1.28 (6H, d), 1.35 (6H, t), 2.33 (3H, s), 3.33 (1H, m), 3.93 (1H, d), 4.17 (4H, dq), 7.00-7.53 (4H, m); IR ($CHCl_3$) 1260 (P=O, s), 1055-1030 (vs) cm^{-1}; Mass (m/e, %) 91 (29.0), 127 (59.0), 155 (54.2), 183 (100.0), 225 (47.0), 274 (32.0), 348 (M, 4.6).

Diethyl 4-methylphenylthio(phenylthio)methanephosphonate (4h). ^1H NMR ($CDCl_3$) δ 1.30 (6H, t), 2.30 (3H, s), 4.17 (4H, dq), 4.27 (1H, d), 6.93-7.53 (9H, m); IR ($CHCl_3$) 1260 (P=O, s), 1050-1025 (vs) cm^{-1}.

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Effect of Carrier Solutions on Particle Retention in Flow Field-Flow Fractionation

Myeong Hee Moon

Department of Chemistry, Kangnung National University, Kangnung 210-702, Korea

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The influence of carrier solutions on particle retention was studied by varying surfactants and ionic strength in flow field-flow fractionation. Experiments were made with five different submicron polystyrene latex standards at three different types of surfactants and seven different ionic strengths. Departures in particle retention from the general theory were observed. At low ionic strength, it is shown that migrating sample zone is clearly lifted away from the ideal equilibrium height and that the repulsive interaction dominates between the particle and the channel wall. As ionic strength increases up to a certain level, particle retention becomes closer to the general theory. Further increase in ionic strength is shown to prolong the retention. An optimum regime of ionic strength is also suggested with the proper choice of surfactants.

Introduction

Field-flow fractionation, a group of separation techniques, is capable of separating and characterizing colloids, polymers, and biological macromolecules.[1~4] FFF techniques utilize external fields (or driving forces) to retain sample components in the separation channel (columns in chromatographic system). Separation in FFF systems is carried out in a thin ribbon-like channel under the application of an external field in the direction perpendicular to the axis of separation flow.[2] The external forces drive sample materials toward the one side of the channel wall (called as accumulation wall) and push the components of different mass or size to distribute at different streampaths of longitudinal flow. The flow moving through the thin channel assumes a laminar type having a parabolic flow profile in which flow velocity is close to