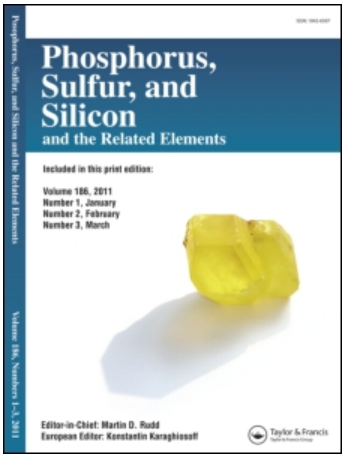

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FACILE SYNTHESIS OF 1-(SUBSTITUTED-ARYL)ALKYLTHIOMETHANEPHOSPHONATES

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FACILE SYNTHESIS OF 1-(SUBSTITUTED-ARYL)ALKYLTHIOMETHANEPHOSPHONATES

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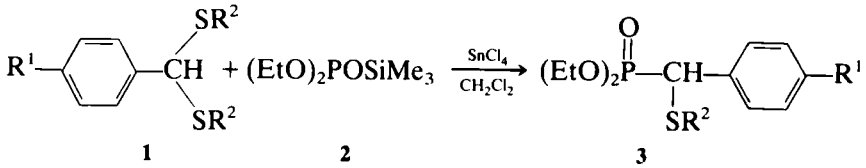
1-(Substituted-aryl)alkylthiomethanephosphonates are prepared by the reaction of arylaldehyde dialkyl thioacetals and diethyl trimethylsilyl phosphite in the presence of stannic chloride under mild conditions.

1-(Substituted-aryl)alkylthiomethanephosphonates **3** are the useful intermediates for the conversion under Wittig–Horner reaction condition into the corresponding α, β-unsaturated sulfide which affords the aromatic ketone by the hydrolysis.[1,2] Until now, 1-(substituted-aryl) alkylthiomethanephosphonates **3** have been obtained by the following methods; addition of dialkyl disulfide, or elemental sulfur and alkyl halide to arylmethanephosphonate carbanion,[3] alkylation of 1-mercaptoarylmethanephosphonate,[2] and Friedel–Crafts reaction of chloro (alkylthio) methanephosphonate.[4] These known methods are successful to some extent but not sufficient both in yield and in reaction conditions.

In the course of our studies on α-heterosubstituted phosphonates we have recently developed a synthesis of 1-alkoxy-1-arylmethanephosphonates[5] which involves the Arbuzov reaction of diethyl trimethylsilyl phosphite with arylaldehyde acetals. In an extension of this work we now wish to report a convenient synthetic method for the preparation of 1-(substituted-aryl)alkylthiomethanephosphonates **3** using arylaldehyde dialkyl thioacetals(**1**) and diethyl trimethylsilyl phosphite(**2**). Diethyl trimethylsilyl phosphite(**2**) reacted with thioacetal(**1**) in the presence of one equivalent stannic chloride to give desired phosphonates **3** in good yields. Compounds **3** were purified by Kugelrohr distillation and characterized by IR-spectra. ^{1}H and ^{31}P NMR spectra, and mass spectroscopy (Table I).



1 **2** **3**

Treatment of thioacetals **1** with the stannic chloride presumably leads to formation of intermediate thionium ions.[6] In a subsequent nucleophilic reaction phosphite **2** reacts with these ions to yield phosphonates **3**.

The advantages of this synthetic method are to synthesize directly from the phosphite, to the easy preparation of starting materials[7] and to proceed satisfactorily with electron withdrawing as well as electron donating para-substituents on the aromatic moiety of thioacetals **1**.

TABLE I

Diethyl 1-(substituted-aryl)alkylthiomethanephosphonates 3a–j

Product[a] No.	R^1	R^2	Yield [%]	b.p.[°C]/torr[b]	Molecular formula[c]	^{1}H-NMR($CDCl_3$/TMS) [ppm]	M.S. m/e (rel. intens.%)	^{31}P-NMR($CDCl_3/H_3PO_4$)[d] [ppm](Lit. value)
3a	H	C_4H_9	80	125–128/0.35	$C_{15}H_{25}O_3PS$ (316.4)	0.71–1.45 (m, 13H), 2.54 (t, J = 7.0 Hz, 2H); 4.01 (dq, J = 7.4 Hz), 4.05 (d, J = 21.5 Hz, 1H); 0.26 (s, 5H)	316 (M^+, 4.3); 228 (51.1); 179 (70.5); 91 (100)	22.2
3b	H	C_2H_5	75	110–112/0.35	$C_{13}H_{21}O_3PS$ (288.4)	1.16, 1.28 (2t, J = 7.2 Hz, 9H); 2.51 (9, J = 7.0 Hz, 2H), 4.05 (d, 21.2 Hz, 1H); 4.07 (dq, J = 7.3 Hz, 4H); 7.26 (s, 4H) 1H); 4.06 (dq, J = 7.4 Hz, 4H); 6.79–7.54 (m, 4H)	288 (M^+, 4.0); 228 (16.5); 151 (100)	22.2 (23.2)[2]
3c	CH_3	C_4H_9	79	143–144/0.35	$C_{16}H_{27}O_3PS$ (330.4)	0.70–1.56 (m, 13H); 2.30 (s, 3H); 2.52 (t, J = 7.0 Hz, 2H); 3.99 (d, J = 20.1 Hz, 1H); 4.04 (dq, J = 7.4 Hz, 4H); 7.00–7.55 (m, 4H)	330 (M^+, 0.9); 242 (68.4); 193 (82.3); 105 (100)	22.3
3d	CH_3	C_2H_5	71	128–133/0.35	$C_{14}H_{23}O_3PS$ (302.4)	1.20, 1.33 (2t, J = 7.8 Hz, 9H); 2.37 (s, 3H), 2.58 (1, J = 7.0 Hz, 2H), 4.10 (d, J = 22.0 Hz, 1H); 4.14 (dq, J = 7.0 Hz, 4H), 6.95–7.55 (m, 4HO)	302 (M^+, 1.6) 242 (41.5) 165 (100)	22.3

3e	OCH_3	C_4H_9	88	146–158/0.30	$C_{16}H_{27}O_4PS$ (346.4)	0.73–1.45 (m, 13H); 2.54 (t, $J = 7.0$ Hz, 2H); 3.79 (s, 3H), 4.04 (d, $J = 20.4$ Hz, 1H); 4.06 (dq, $J = 7.4$ Hz, 4H); 6.97–7.54 (m, 4H)	346 (M^+, 12.3); 258 (43.8); 209 (98.6); 121 (100)	22.0
3f	OCH_3	C_2H_5	81	144–145/0.35	$C_{14}H_{23}O_4PS$ (318.4)	1.17, 1.29 (2t, $J = 7.2$ Hz, 9H); 2.51 (q, $J = 7.0$ Hz, 2H); 3.74 (s, 3H); 4.04 (d, $J = 21.0$ Hz, 1H); 4.06 (dq, $J = 7.3$ Hz, 4H); 6.64–7.47 (m, 4H)	318 (M^+, 4.3); 258 (20.6); 181 (100)	21.8
3g	Cl	C_4H_9	72	136–140/0.30	$C_{15}H_{24}ClO_3PS$ (350.8)	0.74–1.55 (m, 2.53 (t, $J = 7.0$ Hz, 2H); 4.00*d, $J = 18.9$ Hz, 1H); 4.07 (dq, $J = 7.4$ Hz, 4H); 7.41 (s, 4H)	350 (M^+, 0.6), 262 (30.6); 157 (64.6); 155 (40.1); 125 (100)	22.7
3h	Cl	C_2H_5	65	127–129/0.35	$C_{13}H_{20}ClO_3PS$ (322.8)	1.00–1.50 (m, 9H), 2.54 (q, $J = 7.0$ Hz, 2H); 4.14 (dq, $J = 7.3$ Hz, 4H); 4.74 (d, $J = 21.8$ Hz, 1H); 7.41 (s, 4H)	322 (M^+, 1.5), 262 (33.3); 199 (73.6); 185 (100)	21.6
3i	NO_2	C_4H_9	68	140–154/0.30	$C_{15}H_{24}NO_5PS$ (361.4)	0.80–1.60 (m, 13H); 2.56 (t, $J = 7.0$ Hz, 2H); 4.10 (dq, $J = 7.4$ Hz, 4H); 4.13 (d, $J = 20.6$ Hz, 1H), 7.46–8.36 (m, 4H)	361 (M^+, 0.6) 273 (40.5) 136 (100)	20.5
3j	NO_2	C_2H_5	60	140–143/0.35	$C_{13}H_{20}NO_5PS$ (333.3)	1.23, 1.35 (2t, $J = 7.2$ Hz, 9H); 2.59 (q, $J = 7.0$ Hz, 2H); 3.83–4.39 (m, 5H); 7.55–8.34 (m, 4H)	333 (M^+, 0.9) 273 (64.4) 217 (47.5) 196 (100)	20.1

[a] The IR spectra of all products show an absorption at $\nu = 1250\ cm^{-1}$ (s, $p = 0$).
[b] Kugelrohr distillation.
[c] All products gave satisfactory microanalyses (C ± 0.25, H ± 0.24).
[d] The conversion of positive ^{31}P NMR to low field from H_3PO_4 is used.

EXPERIMENTAL

General. The ^{1}H, ^{31}P NMR spectra were obtained on a Varian FT-80A or Bruker AM-200 spectrometer. Standards were tetramethylsilane(TMS) for ^{1}H NMR and 85% H_3PO_4 for ^{31}P NMR. ^{31}P chemical shifts downfield from 85% H_3PO_4 are designated positive. The IR spectra were determined on a Perkin–Elmer Model 283B grating spectrophotometer. Mass spectra were obtained using a HP-5985 mass spectrometer. Microanalyses were performed by the Analytical Lab., KAIST, Korea.

The general experimental procedure is as following. To a stirred solution of thioacetal **1** (2 mmol) in methylene chloride under nitrogen at −78°C is slowly added stannic chloride (2.1 mmol). After 5 min of stirring at −78°C, diethyl trimethylsilyl phosphite **2** (2 mmol) is added into the reaction mixture. The resulting solution is left to slowly return to room temperature for 3–4 h. The reaction mixture is quenched by adding water (5 ml) and stirring for 5 min. The organic layer is separated, dried with magnesium sulfate, and evaporated to leave pale yellow or colourless oil. The product was purified by Kugelrohr distillation.

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