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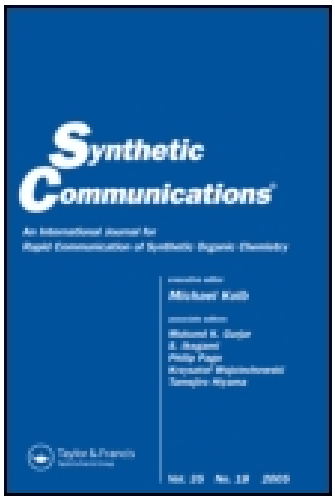

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

An Efficient Synthesis of α-(2,4-Dichloro-phenoxyacetoxy)aryl Methyl Phosphonate Monosodium Salts

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Published online: 21 Aug 2006.

To cite this article: Tao Wang & Hong Wu He (2004) An Efficient Synthesis of α-(2,4-Dichloro-phenoxyacetoxy)aryl Methyl Phosphonate Monosodium Salts, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 34:8, 1415-1423, DOI: 10.1081/SCC-120030691

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SYNTHETIC COMMUNICATIONS®
Vol. 34, No. 8, pp. 1415–1423, 2004

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An Efficient Synthesis of α-(2,4-Dichlorophenoxyacetoxy)aryl Methyl Phosphonate Monosodium Salts

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ABSTRACT

A series of α-(2,4-dichlorophenoxyacetoxy)aryl methyl phosphonate monosodium salts **6** were synthesized by the reaction of the intermediate **5** with sodium iodide under moderate condition. This method was applied to the synthesis of novel phosphonate derivatives containing sensitive groups such as carboxylic ester to acid, base, or water.

Key Words: Phosphonate monosodium salt; Synthesis; Pyruvate dehydrogenase; Carboxylic ester.

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DOI: 10.1081/SCC-120030691 0039-7911 (Print); 1532-2432 (Online)
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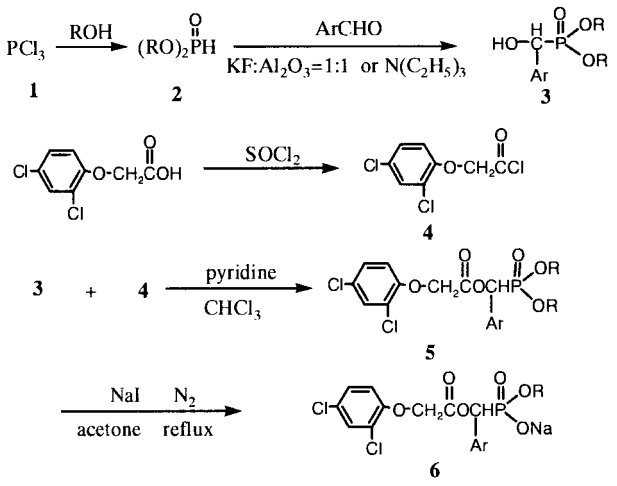
INTRODUCTION

Pyruvate dehydrogenase complex is already known to be a site of pesticide action.[1] For a number of years, we have been engaged in attempts to design agrochemicals using biochemical reasoning. Some substituted phenoxyacetoxyaryl methyl phosphonates have shown herbicidal activities.[2,3] The biological activity of its corresponding phosphonate monosodium salts would be of better herbicidal activity, because the structure of α-oxophosphonate salt is more analogous to the pyruvate which act as the substrate of pyruvate dehydrogenase complex. Recently, we are interested in the synthesis of biologically active α-oxophosphonate monosodium salts. However, they cannot be prepared by using the general method described in the literature.[4] Here, we wish to report a very mild and efficient method to synthesize α-(2,4-dichlorophenoxyacetoxy)aryl methyl phosphonate monosodium salts **6** from the corresponding aryl methyl phosphonates **5**. The title compounds **6** were prepared by the method shown in Sch. 1 and Table 1.

RESULTS AND DISCUSSIONS

Generally, according to the literature,[4] Baillie et al. reported that phosphonate monosodium salts could be obtained by a direct means of converting phosphonate esters in butanone (Sch. 2). However, this method is



Scheme 1.

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Table 1. Preparation of the title compounds **6**.

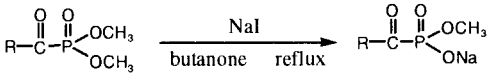
Compounds	R	Ar	Condition (59°C)	Yield (%)
6a	CH_3	C_6H_5	2h	86
6b	CH_3	2,4-$Cl_2C_6H_3$	2h	82
6c	CH_3	*p*-$CH_3OC_6H_4$	4h	88
6d	CH_3	3,4-$OCH_2OC_6H_3$	4h	86
6e	CH_3	*p*-FC_6H_4	3h	79
6f	CH_3	*p*-$CH_3C_6H_4$	2h	78
6g	CH_3	*m*-$NO_2C_6H_4$	3h	85
6h	C_2H_5	C_6H_5	14h	72
6i	C_2H_5	2,4-$Cl_2C_6H_3$	19h	66
6j	C_2H_5	3,4-$OCH_2OC_6H_3$	18h	72
6k	C_2H_5	*p*-FC_6H_4	22h	68
6l	C_2H_5	*p*-$CH_3C_6H_4$	16h	79
6m	C_2H_5	*m*-$NO_2C_6H_4$	10h	71

not applicable to the phosphonates containing sensitive groups such as carboxylic ester to acid, base, water, or temperature.

Attempts to prepare **6a** by direct reaction of sodium monomethyl-1-hydroxy phenyl methyl phosphonate with 2,4-dichloro phenoxy acetic chloride **4** in the presence of pyridine were unsuccessful (Sch. 3).

As described in the literature,[5] we attempted to prepare disodium salt **6a′** by the reaction of C_2H_5ONa with **8**, which can be prepared by dealkylation of *o,o*-dimethyl-α-(2,4-dichlorophenoxyacetoxy)phenyl methyl phosphonate **7** (Sch. 4). Unfortunately, in this case, the ester bond in the phosphonic acid **8** is still too delicate to survive the harsh basic condition by using C_2H_5ONa at higher temperature.

Based on the above considerations, the synthetic route was chosen to prepare the phosphonate monosodium salts **6** (Sch. 1). The experiments showed that the reactions of the compounds **5a–m** with sodium iodide were affected by reaction temperature, base, solvent, and water. We observed that carboxylic ester bond in compounds **5** was easy to cleave by hydrolysis in the presence of base and water at about 60°C. For example, when the title compound **6a** was prepared under basic condition (pH = 9–10) by the reaction in Sch. 1, both by-products **6x** and **6y** were found, which were identified as 2,4-dichloro-



Scheme 2.

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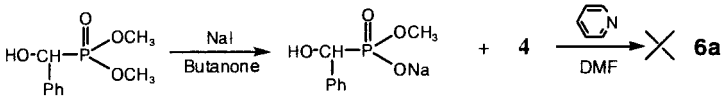


Scheme 3.

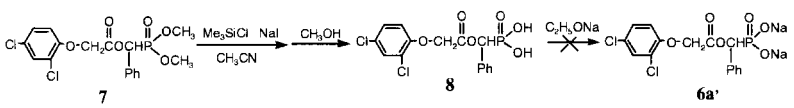
phenoxy acetic acid **6x** and sodium monomethyl-1-hydroxy phenyl methyl phosphonate **6y**, respectively. The reactions were examined in different conditions (Sch. 5, e.g., 1). When refluxing of compound **5g** with oven-dried sodium iodide at 83°C in the presence of butanone, we did not find the corresponding **6g**, but got both by-product **6x** and **6y′** ($R = CH_3$, $Ar = 3\text{-}NO_2C_6H_4$).

We attempted to prepare **6h** by the reaction of **5h** with oven-dried sodium iodide in the presence of butanone for 48 hr, but no **6h** was found, producing both by-product **6x** and by-product **6y″** identified as sodium monoethyl-1-hydroxy phenyl methyl phosphonate instead. However, when the compound **5h** and sodium iodide were dissolved in acetone and stirred and refluxed only for 14 hr, the title compound **6h** was obtained.

Therefore, in the molecular structure of α-(2,4-dichlorophenoxyacetoxy)-aryl methyl phosphonate **5**, the carboxylic ester bond may be more delicate to cleave than phosphonate ester bond in such a hard condition. The formation of the title compounds **6** can be rationalized in terms of direct reaction of the phosphonates **5** with oven-dried sodium iodide in the presence of molecular sieve (4A) in dried acetone under nitrogen for 2–22 hr. The method of the preparation shows following advantageous features: (a) the title compounds **6** can be obtained from **5** in one-step; (b) the reactions only need short time under mild condition by a simple procedure.

EXPERIMENTAL

Melting points (m.p.) were measured on an electrothermal melting-point apparatus and uncorrected; Elemental analysis was performed by Vario EL III elemental analysis; IR spectra were obtained with a Avatar 360 spectrometer; ^{1}H NMR were measured with a Varian XL-300 spectrometer at



Scheme 4.

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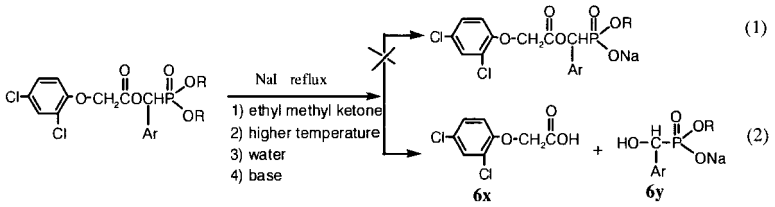

Scheme 5.

300 MHz. Tetramethyl silane (TMS) was used as an internal standard, and chemical shift values are expressed in δ(DMSO) ppm. MS were measured on a Finnigen Trace 2000 spectrometer.

Compounds **3** and **4** were prepared according to the literature.[6,7]

General Procedure for the Synthesis of *o,o*-Dialkyl-α-(2,4-dichlorophenoxyacetoxy)aryl Methyl Phosphonates (5a–m)

A solution of 2,4-dichlorophenoxy acetic chloride **4** (0.022 mol) in trichloromethane (10 mL) was added to stirred mixture of 1-hydroxy aryl methyl phosphonate **3** (0.02 mol) and pyridine (0.022 mol) in trichloromethane (25 mL) at 2–4°C. The resultant mixture was stirred at ambient temperature for 3–5 hr, then all stirred at 40°C for 1–2 hr, washed with 0.1 M hydrochloric acid, saturated sodium hydrogen carbonate solution and brine, dried and evaporated. The residue was chromatographed on silica with 20% acetone in petroleum ether as eluent to give the compound **5** as a yellow liquid or white solid, which was recrystallized from DCM/petroleum ether. Yield: 58–91%.

General Procedure for the Synthesis of Sodium Monomethyl-α-(2,4-dichlorophenoxyacetoxy)aryl Methyl Phosphonates (6a–g)

A solution of *o,o*-dimethyl-α-(2,4-dichlorophenoxyacetoxy)aryl methyl phosphonate (0.02 mol) and oven-dried sodium iodide (0.02 mol) in molecular sieve (4A) dried acetone (40 mL) was stirred and refluxed under nitrogen for 2–4 hr, The solution was evaporated at reduced pressure. The residual solid was recrystallized from dichloromethane to afford the pure product as white solid or crystal (the product was very deliquescent). The salts were isolated directly in 78–88% yields.

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6a. White crystal, m.p. 164–165°C; ^{1}H NMR: 3.29–3.34 (d, 3H, $-OCH_3$, $J = 10.0$ Hz), 4.90–5.09 (q, 2H, $-OCH_2CO-$, $J = 12.6$ Hz), 5.77–5.83 (d, 1H, –OCHP, $J = 12.0$ Hz), 6.98–7.53 (m, 8H, $-C_6H_5$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3042 (Ph–H), 2952, 2846 (C– H), 1715 (C═O), 1601, 1601, 1490 (Ph), 1244 (P═O), 1077 (C–O–C), 1045, 930 (P–O–C), 722 (P–C). MS (m/z): 426 (M^+ 0.1%), 234 (14.35%), 220 (15.98%), 199 (43.15%), 185 (4.30%), 175 (70.19%), 162 (77.72%), 133 (41.88%), 109 (85.39%), 105 (52.92%), 94 (3.78%), 93 (100%), 77 (63.71%), 63 (93.51%). Anal. calcd for $C_{16}H_{14}Cl_2NaO_6P$: C, 44.99; H, 3.30. Found: C, 44.51; H, 3.52.

6b. White solid, m.p. 151–152°C; ^{1}H NMR: 3.35–3.40 (d, 3H, $-OCH_3$, $J = 10.0$ Hz), 4.98 (s, 2H, $-OCH_2CO-$), 6.06–6.12 (d, 1H, –OCHP, $J = 12.0$ Hz), 6.95–7.60 (m, 6H, $-C_6H_3$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3087 (Ph–H), 2952, 2846 (C–H), 1743 (C═O), 1643, 1585, 1485 (Ph), 1217 (P═O), 1079 (C–O–C), 1051, 928 (P–O–C), 744 (P–C). MS (m/z): 494 (M^+ 0.1%), 234 (28.65%), 220 (3.89%) 199 (48.38%), 175 (74.41%), 173 (61.47%), 162 (100%), 133 (28.65%), 109 (36.44%), 94 (1.91%), 93 (3.99%), 63 (72.35%). Anal. calcd for $C_{16}H_{12}Cl_4NaO_6P$: C, 38.74; H, 3.31. Found: C, 38.92; H, 3.28.

6c. White solid, m.p. 109–110°C; ^{1}H NMR: 3.27–3.31 (d, 3H, $-OCH_3$, $J = 8.7$ Hz), 3.72 (s, 3H, CH_3O-Ph), 4.85–5.04 (q, 2H, $-OCH_2CO-$, $J = 11.6$ Hz), 5.69–5.75 (d, 1H, –OCHP, $J = 13.6$ Hz), 6.76–7.54 (m, 7H, $-C_6H_4$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3076 (Ph–H), 2947, 2829 (C–H), 1736 (C═O), 1611, 1514, 1485 (Ph), 1226 (P═O), 1080 (C–O–C), 1051, 932 (P–O–C), 734 (P–C). MS (m/z): 456 (M^+ 0.05%), 234 (32.20%), 220 (13.78%), 199 (57.55%), 175 (44.58%), 162 (100%), 135 (60.88%), 133 (27.57%), 109 (24.13%), 93 (2.04%), 63 (62.19%). Anal. calcd for $C_{17}H_{16}Cl_2NaO_7P$: C, 44.66; H, 3.53. Found: C, 44.58; H, 3.59.

6d. White solid, m.p. 83–85°C; ^{1}H NMR: 3.29–3.34 (d, 3H, $-OCH_3$, $J = 9.7$ Hz), 4.86–5.07 (q, 2H, $-OCH_2CO-$, $J = 13.6$ Hz), 5.67–5.73 (d, 1H, –OCHP, $J = 10.7$ Hz), 5.93 (s, 2H, $-OCH_2OPh$), 6.76–7.53 (m, 6H, $-C_6H_3$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3092 (Ph–H), 2941, 2840 (C–H), 1735 (C═O), 1615, 1503, 1485 (Ph), 1245 (P═O), 1079 (C–O–C), 1038, 934 (P–O–C), 761 (P–C). MS (m/z): 470 (M^+ 0.3%), 234 (15.55%), 220 (9.29%), 199 (28.68%), 175 (35.56%), 162 (28.86%), 149 (24.92%), 133 (69.41%), 109 (86.58%), 94 (1.60%), 93 (10.55%), 63 (83.23%). Anal. calcd for $C_{17}H_{14}Cl_2NaO_8P$: C, 43.34; H, 2.98. Found: C, 43.21; H, 3.07.

6e. White crystal, m.p. 143–144°C; ^{1}H NMR: 3.31–3.36 (d, 3H, $-OCH_3$, $J = 9.7$ Hz), 4.98–5.01 (q, 2H, $-OCH_2CO-$, $J = 4.9$ Hz), 5.76–5.83 (d, 1H, –OCHP, $J = 12.6$ Hz), 7.01–7.52 (m, 7H, $-C_6H_4$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3065 (Ph–H), 2941, 2835 (C–H), 1742 (C═O), 1629, 1559, 1484

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(Ph), 1197 (P═O), 1076 (C–O–C), 1035, 931 (P–O–C), 768 (P–C). MS (m/z): 444 (M^+ 0.05%), 234 (35.34%), 220 (9.86%), 199 (66.23%), 175 (79.06%), 162 (68.35%), 133 (37.95%), 123 (72.38%), 109 (100%), 94 (6.15%), 93 (80.78%), 63 (66.55%). Anal. calcd for $C_{16}H_{13}Cl_2FNaO_6P$: C, 43.17; H, 2.94. Found: C, 43.08; H, 3.23.

6f. White solid, m.p. >108°C (decompound); ^{1}H NMR: 2.25 (s, 3H, $-CH_3Ph$), 3.31–3.35 (d, 3H, $-OCH_3$, $J = 9.7$ Hz), 4.98 (s, 2H, $-OCH_2CO-$), 5.76–5.82 (d, 1H, –OCHP, $J = 12.6$ Hz), 7.03–7.51 (m, 7H, $-C_6H_4$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3077 (Ph–H), 2978, 2845 (C–H), 1757 (C═O), 1612, 1537, 1487 (Ph), 1213 (P═O), 1122 (C–O–C), 1122, 930 (P–O–C), 765 (P–C). MS (m/z): 440 (M^+ 0.8%), 234 (25.20%), 220 (19.40%), 199 (29.57%), 175 (60.62%), 162 (100%), 133 (19.29%), 119 (10.64%), 109 (35.91%), 94 (3.93%), 93 (9.61%), 63 (33.03%). Anal. calcd for $C_{17}H_{16}Cl_2NaO_6P$: C, 46.28; H, 3.66. Found: C, 46.19; H, 3.58.

6g. White crystal, m.p. 98–99°C; ^{1}H NMR: 3.36–3.41 (d, 3H, $-OCH_3$, $J = 9.7$ Hz), 5.04–5.09 (q, 2H, $-OCH_2CO-$, $J = 11.7$ Hz), 5.89–5.95 (d, 1H, –OCHP, $J = 12.6$ Hz), 7.03–8.16 (m, 7H, $-C_6H_4$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3076 (Ph–H), 2958, 2857 (C–H), 1759 (C═O), 1632, 1535, 1484 (Ph), 1217 (P═O), 1075 (C–O–C), 1040, 932 (P–O–C), 728 (P–C). MS (m/z): 471 (M^+ 0.3%), 234 (33.09 %), 220 (15.49%), 199 (61.55%), 175 (48.66%), 162 (100%), 150 (51.60%), 133 (33.49%), 109 (32.25%), 94 (1.38%), 93 (2.91%), 63 (64.93%). Anal. calcd for $C_{16}H_{13}Cl_2NNaO_8P$: C, 40.70; H, 2.78; N, 2.97. Found: C, 40.61; H, 2.89; N, 3.01.

General Procedure for the Synthesis of Sodium Monoethyl-α-(2,4-dichlorophenoxyacetoxy)aryl Methyl Phosphonates (6h–m)

A solution of *o,o*-diethyl-α-(2,4-dichlorophenoxyacetoxy)aryl methyl phosphonate (0.02 mol) and oven-dried sodium iodide (0.02 mol) was refluxed for 10–22 hr in molecular sieve (4A) dried acetone (40 mL) under nitrogen. The solution was evaporated at reduced pressure. The residual solid was recrystallized from dichloromethane to afford the pure product as white solid or crystal (the product was very deliquescent). The salts were isolated directly in 66–79% yields.

6h. White solid, m.p. > 261°C (decompound); ^{1}H NMR: 1.01–1.07 (t, 3H, $-OCH_2CH_3$, $J = 7.0$ Hz), 3.64–3.76 (m, 2H, $-OCH_2CH_3$), 4.91–5.07 (q, 2H, $-OCH_2CO-$, $J = 16.8$ Hz), 5.72–5.76 (d, 1H, –OCHP, $J = 12.2$ Hz), 7.01–7.67 (m, 8H, $-C_6H_5$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3072 (Ph–H), 2947, 2858 (C–H), 1732 (C═O), 1617, 1530, 1487 (Ph), 1242 (P═O), 1081 (C–O–C), 1081, 946 (P–O–C), 741 (P–C). MS (m/z):

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440 (M^+ 0.60%), 220 (3.67%), 133 (4.21%), 127 (100.0%), 75 (6.75%), 73 (9.78%). Anal. calcd for $C_{17}H_{16}Cl_2NaO_6P$: C, 46.28; H, 3.66. Found: C, 46.09; H, 3.73.

6i. White crystal, m.p. $> 258^\circ$C (decompound); ^{1}H NMR: 1.12–1.17 (t, 3H, $-OCH_2CH_3$, $J = 7.1$ Hz), 3.82–3.91 (m, 2H, $-OCH_2CH_3$), 5.00 (s, 2H, $-OCH_2CO-$), 5.05–5.10 (d, 1H, $-OCHP$, $J = 13.5$ Hz), 7.01–7.77 (m, 6H, $-C_6H_3$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3054 (Ph–H), 2952, 2862 (C–H), 1712 (C=O), 1613, 1539, 1450 (Ph), 1224 (P=O), 1066 (C–O–C), 1032, 943 (P–O–C), 760 (P–C). MS (m/z): 508 (M^+ 0.18%), 220 (5.69%), 133 (8.90%), 127 (100.0%), 75 (8.691%), 73 (23.78%). Anal. calcd for $C_{17}H_{14}Cl_4NaO_6P$: C, 40.03; H, 2.77. Found: C, 39.91; H, 2.64.

6j. White solid, m.p. 201–203°C; ^{1}H NMR: 1.20–1.25 (t, 3H, $-OCH_2CH_3$, $J = 7.6$ Hz), 3.62–3.67 (d, 3H, $-OCH_2CH_3$), 4.84–4.98 (q, 2H, $-OCH_2CO-$, $J = 14.8$ Hz), 5.67–5.71 (d, 1H, $-OCHP$, $J = 12.2$ Hz), 5.96 (s, 2H, $-OCH_2OPh$), 6.86–7.63 (m, 6H, $-C_6H_3$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3078 (Ph–H), 2958, 2846 (C–H), 1729 (C=O), 1627, 1534, 1489 (Ph), 1232 (P=O), 1080 (C–O–C), 1035, 946 (P–O–C), 765 (P–C). MS (m/z): 484 (M^+ 0.80%), 220 (4.67%), 133 (6.31%), 127 (100.0%), 75 (9.55%), 73 (7.78%). Anal. calcd for $C_{18}H_{16}Cl_2NaO_8P$: C, 44.56; H, 3.32. Found: C, 44.47; H, 3.21.

6k. White solid, m.p. $>276^\circ$C (decompound); ^{1}H NMR: 1.00–1.05 (t, 3H, $-OCH_2CH_3$, $J = 7.0$ Hz), 3.63–3.73 (m, 2H, $-OCH_2CH_3$), 4.93–5.11 (q, 2H, $-OCH_2CO-$, $J = 17.6$ Hz), 5.78–5.82 (d, 1H, $-OCHP$, $J = 12.5$ Hz), 7.03–7.61 (m, 7H, $-C_6H_4$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3078 (Ph–H), 2941, 2847 (C–H), 1730 (C=O), 1611, 1528, 1484 (Ph), 1219 (P=O), 1070 (C–O–C), 1034, 943 (P–O–C), 772 (P–C). MS (m/z): 458 (M^+ 0.18%), 220 (2.69%), 133 (2.97%), 127 (100.0%), 75 (7.51%), 73 (24.78%). Anal. calcd for $C_{17}H_{15}Cl_2FNaO_6P$: C, 44.47; H,3.29. Found: C, 44.28; H, 3.38.

6l. White solid, m.p. $>265^\circ$C (decompound); ^{1}H NMR: 0.98–1.03 (t, 3H, $-OCH_2CH_3$, $J = 7.1$ Hz), 2.26 (s, 3H, $-CH_3Ph$), 3.60–3.70 (m, 2H, $-OCH_2CH_3$), 4.90–5.06 (q, 2H, $-OCH_2CO-$, $J = 16.3$ Hz), 5.73–5.77 (d, 1H, $-OCHP$, $J = 12.5$ Hz), 7.03–7.59 (m, 7H, $-C_6H_4$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3056 (Ph–H), 2947, 2841 (C–H), 1729 (C=O), 1629, 1536, 1482 (Ph), 1281 (P=O), 1077 (C–O–C), 1032, 948 (P–O–C), 759 (P–C). MS (m/z): 454 (M^+ 1.32%), 220 (1.69%), 133 (4.59%), 127 (100.0%), 75 (18.51%), 73 (31.21%). Anal. calcd for $C_{18}H_{18}Cl_2NaO_6P$: C, 47.49; H,3.99. Found: C, 47.28; H, 4.12.

6m. White solid, m.p. 192–193°C; ^{1}H NMR: 1.01–1.06 (t, 3H, $-OCH_2CH_3$, $J = 7.0$ Hz), 3.67– 3.75 (m, 2H, $-OCH_2CH_3$), 4.98–5.20 (q, 2H, $-OCH_2CO-$, $J = 19.9$ Hz), 5.89–5.93 (d, 1H, $-OCHP$, $J = 13.1$ Hz), 7.07–8.18 (m, 7H, $-C_6H_4$, $-C_6H_3$). IR (KBr) υ_{max} (cm^{-1}): 3043

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(Ph–H), 2971, 2859 (C–H), 1730 (C═O), 1624, 1530, 1482 (Ph), 1222 (P═O), 1077 (C–O–C), 1047, 946 (P–O–C), 699 (P–C). MS (m/z): 485 (M^+ 0.09%), 220 (5.19%), 199 (1.55%), 175 (8.06%), 162 (12.84%), 150 (6.30%), 145 (29.10%), 133 (9.09%), 127 (100.0%), 111 (6.31%), 109 (8.25%), 75 (18.51%), 74 (31.21%), 63 (49.93%). Anal. calcd for $C_{17}H_{15}Cl_2NNaO_8P$: C, 42.00; H, 3.11; N, 2.88. Found: C, 41.87; H, 3.20; N, 3.01.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support of this work by National Natural Science Foundation of China (Project No: 29572045, 20072008, 20372023).

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Received in Japan August 18, 2003

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