Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 2608–2613
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and herbicidal activities of methyl-1-(2,4-dichlorophenoxyacetoxy)alkylphosphonate monosalts

Hong Wu He *, Tao Wang [1], Jun Lin Yuan

Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, Institute of Organic Synthesis, Central China Normal University, Wuhan, Hubei 430079, PR China

Received 20 December 2004; accepted 31 January 2005
Available online 12 April 2005

Abstract

A series of 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonic acid dimethyl esters **5** and its corresponding phosphonate monosalts **6** were synthesized as potential herbicide. The phosphonate monosalts can be prepared from 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonic acid dimethyl esters **5**, which were synthesized by the condensation of *O*,*O*-dimethyl-1-hydroxyalkylphosphonates with dichlorophenoxyacetic chloride. This method provides a simple and efficient procedure for the synthesis of phosphonate derivatives containing sensitive groups to acid, base or water such as carboxylate ester bond; and the herbicidal activity of title compounds was evaluated in a set of experiments in greenhouse. Most of the compounds exhibited notable herbicidal activity.

Keywords: Alkylphosphonate; Monosalt; 1-Hydroxyalkylphosphonate; Synthesis; Herbicidal activity

1. Introduction

One approach to design an inhibitor of pyruvate dehydrogenase (PDH) with a novel structure by using biochemical reasoning was attempted. A series of α-oxophosphonic acid derivatives have been investigated in recent years [1]. Some substituted phenoxyacetoxyalkylphosphonates have shown good herbicide activities and demonstrated as an inhibitor of PDH in our previous work [2,3]. Its corresponding phosphonate monosalts would be of better herbicidal activity, because the structure of the salt is more analogous to the pyruvate which acts as the substrate of pyruvate dehydrogenase complex. In order to find new phosphonate derivatives with better herbicidal activity, the sodium and potassium structural unit was introduced into phosphonates molecules, so we are interested in extending our investigations to a novel series of methyl 1-(dichlorophenoxyacetoxy)alkylphosphonate monosalts and finding a mild and efficient method for conversion of dimethyl phosphonates to corresponding phosphonate monosalts. Here we report the preparation of 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonate monosalts and their herbicidal activity against *Echinochloa crusgalli* Beava, *Digitaria sanguinalis* Scop, *Brassica napus* L., *Amaranthus retroflerus* L., and *Medicago sativa* L.

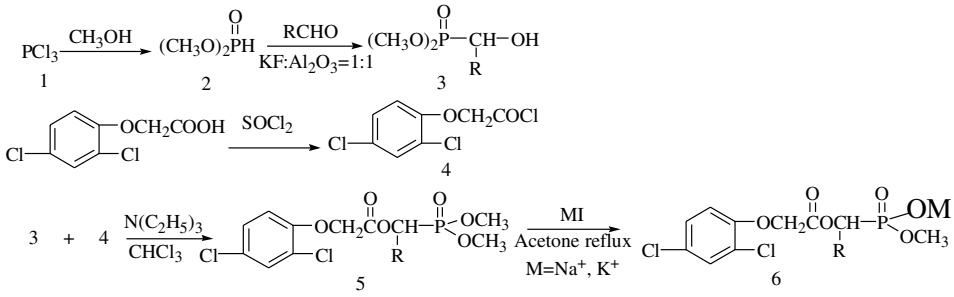
2. Results and discussion

2.1. Synthesis of 1-(2,4-dichlorophenoxyacetoxy)-alkylphosphonate monosalts

The title compounds were synthesized by means of the multi-step procedure outlined in Scheme 1.

* Corresponding author. Tel./fax: +86 27 67867960.
E-mail addresses: hel208@public.wh.hb.cn, he1208@mail.ccnu.edu.cn (H.W. He).
[1] Present address: Department of Chemistry, Yichun University, Yichun 336000, PR China.

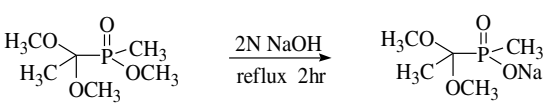
0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.01.061



Scheme 1.

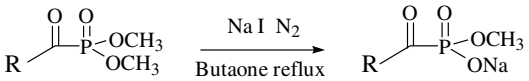
We chose a convenient route to obtain the title compounds **6a**–**j** starting from dimethyl phosphite, which was used directly as obtained commercially or prepared by the reaction of phosphorus trichloride and methanol. Dimethyl phosphite reacted with aldehydes to give *O*,*O*-dimethyl-1-hydroxyalkylphosphonates **3**. The title compounds can be obtained from 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonic acid dimethyl esters **5**, which were prepared by the condensation of *O*,*O*-dimethyl-1-hydroxyalkylphosphonates **3** with dichlorophenoxyacetic chloride **4**.

Phosphonate or phosphinate monosalts could be generally synthesized from corresponding phosphonate or phosphinate derivatives by several procedures [4], such as some phosphinate salts could be obtained by a direct means of converting the phosphinate ester into the corresponding phosphinate salts in 2N sodium hydroxide solution (Eq. (1)). However, the method is not applicable to prepare the phosphonates containing sensitive groups to acid, base, water or temperature such as carboxylate ester group. We failed to obtain the title compounds by direct reaction of converting the phosphonate into the corresponding phosphonate salts in sodium hydroxide solution. We observed that carboxylate ester bond in 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonates **5** or title compounds **6** were easily cleaved by hydrolysis in the presence of base and water at about 60 °C. For example, when the title compound **6b** was prepared under basic (pH 9–10) condition by the reaction in Scheme 1, both methyl-1-hydroxyethylphosphonate monosodium and 2,4-dichlorophenoxyacetic acid as the by-product were found and identified, respectively.



(1)

We also attempted to prepare the title compound **6** by a direct reaction of 1-hydroxyalkylphosphonates monosalt with 2,4-dichlorophenoxyacetic chloride in the presence of pyridine, but unfortunately it was not a good way to prepare the title compounds in better yields. Therefore, as described in the literature [4] (Eq. (2)), the metallic iodide appears to be the best choice for the preparation of phosphonate monosalts from corresponding phosphonates.



(2)

Based on the above considerations, the synthetic route (Scheme 1) was chosen to prepare the phosphonate monosalts. The experiment showed that the reactions of the compounds **5a**–**f** with sodium iodide or potassium iodide were affected by reaction temperature, base, solvent and water. We attempted to prepare the title compound **6h** by the reaction of **5h** with oven-dried potassium iodide in the presence of butanone for 36 h, but no title compound **6h** was found, only producing corresponding methyl-1-hydroxyethylphosphonate monopotassium and 2,4-dichlorophenoxyacetic acid as by-product instead. However, the compound **5h** and potassium iodide were dissolved in acetone and the solution stirred and refluxed only for 12 h, the title compound **6h** could be obtained.

Therefore, in the molecular structure of *O*,*O*-dimethyl-1-(2,4-dichlorophenoxyacetoxy)alkylphosphonates, the carboxylate ester bond may be more delicate to cleave than phosphonate ester bond in such a hard condition. The preparation of the title compounds **6** can be rationalized in terms of direct reaction of the phosphonates **5a**–**f** with sodium iodide or potassium iodide in dried acetone under nitrogen for 3–14 h (see Table 1). This method provides a simple and efficient procedure for the synthesis of phosphonate derivatives containing sensitive groups to acid, base or water such as carboxylate ester.

All of the title compounds **6** were confirmed by ^{1}H NMR, IR, MS and elementary analysis. In the ^{1}H NMR spectra of **6**: both the protons in the P–C moiety and P–OCH_3 moiety display doublets, which is due to couplings to the phosphorus. The IR spectra of all compounds showed normal stretching absorption bands, indicating the existence of the Ph–H (~2950 cm^{-1}), C=O (~1720 cm^{-1}), C=C (~1620, ~1450 cm^{-1}), P=O (~1260 cm^{-1}), P–O–C (~1050 cm^{-1}) and P–C (~750 cm^{-1}). The EI mass spectra of compound **6a**–**f**

gave weak molecular ion peaks. All the fragmentation ions of **6a**–**f** were consistent with the structure and can be clearly assigned.

2.2. Herbicidal activities

The herbicidal activity of title compounds **6a**–**j** was evaluated at a dose of 1.5 a.i. kg/ha in a set of experiments in greenhouse. They were tested for pre-emergence and post-emergence inhibitory effect against *E. crusgalli* Beava (barngard grass), *D. sanguinalis* Scop (ascendant crabgrass), *B. napus* L. (rape), *A. retroflerus* L. (amaranth), and *M. sativa* L. (clover).

Plastic pots were packed with sandy clay loam soil and water was added up to 3 cm in depth. In the pots, seeds of plant were sown, a diluted suspension of each compound containing acetone and Tween 80 was applied into the pots at 1.5 a.i. kg/ha, 5 days later, the pre-emergence herbicidal activity against each weed was visually evaluated. The solution of the chemicals tested was applied to the foliage of plants grown at 2–3 leaves stage with a sprayer at the rate of 1.5 a.i. kg/ha with a spelling volume of 1000 L/ha. Visual assessment was conducted 15 days after treatment on a scale of values of zero (no effect) and 100 (dead). The post-emergence herbicidal activity against each weed was evaluated. Each experiments was replicated two times. The results are listed in Table 2.

As seen from Table 2, most of the synthesized compounds displayed notable herbicidal activity against the growth of the tested plants at a dose of 1.5 a.i. kg/ha. Compounds **6a**, **6b**, **6d**, **6e**, **6h**, and **6i** showed 90–100% inhibitory effect against dicotyledon: *B. napus* L., *A. retroflerus* L., and *M. sativa* L. for both pre-emergence and post-emergence. And those compounds also exhibited good inhibitory activity against monocotyledon: *E. crusgalli* Beava, *D. sanguinalis* Scop for pre-emergence. The results showed that compounds **6**, except **6c** and **6j**, influenced the growth of *E. crusgalli* Beava, *D. sanguinalis* Scop in pre-emergence more strongly than did in post-emergence. Especially, compounds **6f** showed 100% inhibitory effect on the growth of all tested plants for pre-emergence. The significant activities against most tested plants of compound **6g** were also noted. According to the results of herbicidal assays, there is a need for testing further the herbicidal activity of compounds **6a**, **6b**, **6d**, **6e**, **6h**, **6i** and **6f** at lower concentrations.

Table 1
Preparation of title compounds **6a**–**j**

Compound	M	R	Formula	m.p. (°C)	r.t. (h)	Yield (%)
6a	Na^+	H	$C_{10}H_{10}Cl_2NaO_6P$	183–184	3	81
6b	Na^+	CH_3	$C_{11}H_{12}Cl_2NaO_6P$	46–47	3	84
6c	Na^+	C_2H_5	$C_{12}H_{14}Cl_2NaO_6P$	81–83	4	64
6d	Na^+	*n*-C_3H_7	$C_{13}H_{16}Cl_2NaO_6P$	110–112	4	51
6e	Na^+	*n*-C_4H_9	$C_{14}H_{18}Cl_2NaO_6P$	163–165	4	52
6f	Na^+	CCl_3	$C_{11}H_9Cl_5NaO_6P$	121–123	3	65
6g	K^+	H	$C_{10}H_{10}Cl_2KO_6P$	162–164	10	61
6h	K^+	CH_3	$C_{11}H_{12}Cl_2KO_6P$	168–170	12	54
6i	K^+	C_2H_5	$C_{12}H_{14}Cl_2KO_6P$	171–173	12	52
6j	K^+	*n*-C_3H_7	$C_{13}H_{16}Cl_2KO_6P$	146–149	14	43

Table 2
Inhibitory effect of compounds **6a**–**j** on the growth of plants

No.	Pre-emergence (%)[a]					Post-emergence (%)[a]				
	[b]*Ech*	*Dig*	*Bra*	*Ama*	*Med*	*Ech*	*Dig*	*Bra*	*Ama*	*Med*
6a	84.6	90.3	96.6	96.6	100	28.0	28.6	97.7	100	92.5
6b	89.5	100	98.1	100	100	6.20	38.2	100	100	100
6c	0.00	80.9	57.5	91.0	11.9	6.90	24.0	7.10	96.2	94.2
6d	94.1	96.8	98.1	99.0	100	38.4	26.5	100	93.5	100
6e	97.6	96.8	99.0	98.0	100	48.8	51.0	100	100	100
6f	100	100	100	100	100	13.9	8.00	79.4	96.2	100
6g	79.2	98.1	91.4	83.1	96.0	41.3	70.3	84.6	100	58.3
6h	97.2	95.1	100	98.5	96.0	52.2	60.0	100	100	100
6i	100	96.5	98.8	90.0	91.0	82.6	55.0	94.3	95.5	96.0
6j	31.2	35.2	37.0	18.6	10.2	33.8	38.9	42.6	38.5	91.2

[a] Inhibitory effect (%): inhibitory effect of compounds **6a**–**j** on the growth of plants at a dose of 1.5 a.i. kg/ha, measured as percentage change in each plant weight compared to that of the control, such as 0% (no effect or not significantly different from control), 100% (completely killed).
[b] *Ech: Echinochloa crusgalli* Beava; *Dig: Digitaria sanguinalis* Scop; *Bra: Brassica napus* L. *Ama: Amaranthus retroflerus* L.; *Med: Medicago sativa.*

3. Conclusion

1-(2,4-Dichlorophenoxyacetoxy)alkylphosphonate monosalts can be prepared with considerable yield from corresponding phosphonates avoiding the cleavage of carboxylate ester bond in compounds by using sodium iodide or potassium iodide under a moderate condition, which provides an efficient synthesis of 1-(substituted phenoxyacetoxy)alkylphosphonate salts containing carboxylic ester group. The test for herbicidal activities in greenhouse showed that the synthesized compounds exhibited notable herbicidal activity and the possibility that the title compounds may be of potential utility as herbicides, the results of which proved that we can obtain herbicidal active compounds by the biorational design of molecules.

4. Experimental

All the solvents must be absolutely anhydrous. Phosphorous trichloride, triethylamine and thionyl chloride should be distilled before use. Potassium fluoride, alumina and sodium iodide should be dried in an oven before the reaction. A dried and inert atmosphere is required for the preparation of compound **6**. Column chromatography was carried out with Merck silica gel (230–400 Mesh). Thin layer chromatography (TLC) was performed on silica gel GF-254 aluminum. ^{1}H NMR were recorded on Varian XL-300 spectrometer at 300 MHz, using tetramethylsilane as internal standard. Chemical shifts (δ) are given in (DMSO) ppm, coupling constants (J) in Hz and multiplicities are implicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), and m (multiplet). IR spectra were recorded by a Perkin–Elmer-983 spectrometer, peaks area reported in cm^{-1} with indicated relative intensities: s (strong, 67–100%), m (medium, 34–66%), and w (weak, 0–33%). MS were measured on a Finnigen TRACE spectrometer and API2000LC/MS. Elemental analyses were performed by Vario EL III elemental analysis. Melting points (m.p.) were measured on an Electrothermal melting-point apparatus and uncorrected. The IUPAC names were obtained using the software Chemdraw Ultra, version 7.0.1.

4.1. The preparation of dimethyl phosphite (*2*)

Dimethyl phosphite was used directly as obtained commercially or prepared according to the literature [5].

4.2. The preparation of *O,O*-dimethyl-1-hydroxylalkylphosphonates (*3*)

O,O-Dimethyl-1-hydroxyalkylphosphonates (**3**) could be prepared by addition of dimethylphosphite (**2**) and several kinds of aldehydes using potassium fluoride and alumina (mass ratio is 1:1) as catalyst in yield of 67–94% according to the literature [6,7].

4.3. The preparation of 2,4-dichlorophenoxyacetic chloride (*4*)

Compound **4** was prepared according to the literature [8].

4.4. General procedure for the preparation of 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonic acid dimethyl esters (*5*)

A solution of 2,4-dichlorophenoxyacetic chloride **4** (0.022 mol) in trichloromethane (10 ml) was added to stirred mixture of 1-hydroxyalkylphosphonate **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 h, then all stirred at 40 °C for 1–2 h, washed with 0.1 M hydrochloric acid, saturated sodium hydrogen carbonate solution and brine, dried and evaporated. The residue was purified by column chromatography on silica gel and eluted with petroleum ether/acetone (2:1, v/v) to give the corresponding pure title compounds **5** as a yellow liquid or white solid. Yield: 58–89%.

4.5. General procedure for the preparation of methyl-1-(2,4-dichlorophenoxyacetoxy)alkylphosphonate monosalts (*6*)

A solution of *O,O*-dimethyl-1-(2,4-dichlorophenoxyacetoxy)alkylphosphonates (0.02 mol) and oven-dried sodium iodide or potassium iodide (0.02 mol) in molecular sieve (4 Å) dried acetone (40 ml) was stirred and refluxed under nitrogen for 3–14 h. 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 43–84% yields.

4.5.1. *O*-Methyl-1-(2,4-dichlorophenoxyacetoxy)-methylphosphonate monosodium (*6a*)

Compound **6a** was isolated as a white solid (81% yield): m.p. = 183–184 °C; IR (neat cm^{-1}): 3092 (νPh–H), 2948 (νC–H), 1770 (νC=O), 1224 (νP=O), 1102 (νC–O–C), 1046 (νP–O–C), 766 (νP–C); ^{1}H NMR (δ/ppm): 3.33(d, $^3J_{HP}$ = 10.02 Hz, 3H, –OCH_3), 4.05 (d, $^2J_{HP}$ = 8.28 Hz, 2H, –OCH_2P), 4.93 (s, 2H, –OCH_2-CO–), 7.09–7.59 (m, 3H, –C_6H_3); MS *m/z* (ion, rel. int.): 350 (M^+ 0.5), 234 (50.94), 220 (5.91) 199 (87.53), 175 (72.13), 162 (100), 145 (33.49), 133 (35.61), 111 (44.89), 109 (36.72), 98 (51.62), 94 (2.87), 93 (2.29), 75

(46.65), 74 (38.74), 63 (92.49), 44 (84.65). Anal. Calc. for $C_{10}H_{10}Cl_2NaO_6P$: C, 34.21, H, 2.87. Found: C, 34.46, H, 3.13%.

4.5.2. O-Methyl-1-(2,4-dichlorophenoxyacetoxy)-ethylphosphonate monosodium (**6b**)

Compound **6b** was isolated as a white solid (84% yield): m.p. = 46–47 °C; IR (neat cm^{-1}): 3008 (*v*Ph–H), 2947 (*v*C–H), 1754 (*v*C=O), 1178 (*v*P=O), 1070 (*v*C–O–C), 1045 (*v*P–O–C), 795 (*v*P–C); ^1H NMR (δ/ppm): 1.26 (q, $^3J_{HH}$ = 8.00 Hz, 3H, $-CH_3$), 3.35 (d, $^3J_{HP}$ = 10.00 Hz, 3H, $-OCH_3$), 4.84 (s, 2H, $-OCH_2$-CO–), 4.89 (d, $^2J_{HP}$ = 10.20 Hz, 1H, –OCHP), 7.02–7.54 (m, 3H, $-C_6H_3$); MS *m*/*z* (ion, rel. int.): 364 (M^+ 0.2), 234 (2.59), 220 (14.03), 199 (4.28), 175 (16.09), 162 (100), 145 (10.90), 133 (14.30), 123 (2.91), 111 (14.80), 109 (25.85), 98 (28.36), 94 (1.09), 93 (18.56), 75 (13.45), 74 (10.55), 63 (40.42), 44 (26.29); LC-MS *m*/*z* (ion, rel. int.): 341(M^+ −23, 11.44), 219 (73.8), 161(100), 139(67.24), 127(22.49), 387 (M^+ +23, 22.87), 364 (M^+ 9.35), 175 (32.78). Anal. Calc. for $C_{11}H_{12}Cl_2NaO_6P$: C, 36.19, H, 3.31. Found: C, 35.98, H, 3.26%.

4.5.3. O-Methyl-1-(2,4-dichlorophenoxyacetoxy)-propylphosphonate monosodium (**6c**)

Compound **6c** was isolated as a light yellow solid (64% yield): m.p. = 81–83 °C; IR (neat cm^{-1}): 3015 (*v*Ph–H), 2948 (*v*C–H), 1738 (*v*C=O), 1198 (*v*P=O), 1090 (*v*C–O–C), 1050 (*v*P–O–C), 742 (*v*P–C); ^1H NMR (δ/ppm): 0.84 (t, $^3J_{HH}$ = 7.41 Hz, 3H, $-CH_2CH_3$), 1.55–1.86 (m, 2H, $-CH_2CH_3$), 3.35 (d, $^3J_{HP}$ = 9.72 Hz, 3H, $-OCH_3$), 4.79 (d, $^2J_{HH}$ = 9.87 Hz, $1H^a$, $-OCH_2CO-$), 4.84 (d, $^2J_{HH}$ = 11.40 Hz, $1H^b$, $-OCH_2CO-$), 5.01 (d, $^2J_{HP}$ = 16.59 Hz, 1H, –OCHP), 7.07–7.59 (m, 3H, $-C_6H_3$); MS *m*/*z* (ion, rel. int.): 378 (M^+ 0.1), 234 (14.35), 220 (15.98), 199 (43.15), 185 (4.30), 175 (70.19), 162 (77.72), 145 (43.19), 133 (41.88), 111 (61.57), 109 (85.39), 105 (52.92), 98 (33.16), 94 (3.78), 93 (100), 77 (63.71), 75 (40.19), 74 (37.69), 63 (93.51), 44 (52.01). Anal. Calc. for $C_{12}H_{14}Cl_2NaO_6P$: C, 38.02, H, 3.72, Found: C, 37.87, H, 3.46%.

4.5.4. O-Methyl-1-(2,4-dichlorophenoxyacetoxy)-butylphosphonate monosodium (**6d**)

Compound **6d** was isolated as a light yellow solid (51% yield): m.p. = 110–112 °C; IR (neat cm^{-1}): 3009 (*v*Ph–H), 2950 (*v*C–H), 1740 (*v*C=O), 1188 (*v*P=O), 1086 (*v*C–O–C), 1048 (*v*P–O–C), 756 (*v*P–C); ^1H NMR (δ/ppm): 0.83 (t, $^3J_{HH}$ = 7.39 Hz, 3H, $-CH_2CH_2CH_3$), 1.15–1.39 (m, 2H, $-CH_2CH_2CH_3$), 1.58–1.74 (m, 2H, $-CH_2CH_2CH_3$), 3.35 (d, $^3J_{HP}$ = 9.72 Hz, 3H, $-OCH_3$), 4.83 (d, $^2J_{HH}$ = 16.57 Hz, $1H^a$, $-OCH_2CO-$), 4.96(d, $^2J_{HH}$ = 16.56 Hz, $1H^b$, $-OCH_2CO$-); 5.02 (d, $^2J_{HP}$ = 9.90 Hz, 1H, –OCHP), 7.07–7.59 (m, 3H, $-C_6H_3$); MS *m*/*z* (ion, rel. int.): 392 (M^+ 0.05), 234 (41.23), 220 (11.01) 199 (83.16), 175 (70.88), 162 (100), 145 (33.53), 139 (88.36), 133 (33.46), 111 (72.03), 109 (35.91), 98 (32.18), 94 (0.93), 93 (7.61), 75 (54.97), 74 (40.70), 63 (63.03), 44 (31.06). Anal. Calc. for $C_{13}H_{16}Cl_2NaO_6P$: C, 39.72, H, 4.10, Found: C, 39.28, H, 3.86%.

4.5.5. O-Methyl-1-(2,4-dichlorophenoxyacetoxy)-pentylphosphonate monosodium (**6e**)

Compound **6e** was isolated as a light yellow solid (52% yield): m.p. = 163–165 °C; IR (neat cm^{-1}): 3012 (*v*Ph–H), 2947 (*v*C–H), 1743 (*v*C=O), 1186 (*v*P=O), 1079 (*v*C–O–C), 1054 (*v*P–O–C), 748 (*v*P–C); ^1H NMR (δ/ppm): 0.83 (t, $^3J_{HH}$ = 6.63 Hz, 3H, $-CH_2CH_2CH_2CH_3$), 1.14–1.28 (m, 4H, $-CH_2CH_2CH_2CH_3$), 1.58–1.74 (m, 2H, $-CH_2CH_2CH_2CH_3$), 3.35 (d, $^3J_{HP}$ = 9.00 Hz, 3H, $-OCH_3$), 4.83(d, $^2J_{HH}$ = 16.53 Hz, $1H^a$, $-OCH_2CO-$), 4.98(d, $^2J_{HH}$ = 16.53 Hz, $1H^b$, $-OCH_2CO-$); 5.04 (d, $^2J_{HP}$ = 9.80 Hz, 1H, –OCHP), 7.02–7.56 (m, 3H, $-C_6H_3$); MS *m*/*z* (ion, rel. int.): 406 (M^+ 0.03), 234 (7.83), 220 (5.33) 199 (11.98), 175 (21.39), 162 (89.87), 145 (8.35), 142 (100), 139 (77.85), 133 (13.17), 111 (34.68), 109 (6.67), 98 (31.62), 94 (0.29), 93 (0.88), 75 (30.77), 74 (20.51), 63 (47.52), 44 (9.53). Anal. Calc. for $C_{14}H_{18}Cl_2NaO_6P$: C, 41.30, H, 4.46. Found: C, 41.04, H, 4.18%.

4.5.6. O-Methyl-1-(2,4-dichlorophenoxyacetoxy)2,2,2-trichloroethylphosphonate monosodium (**6f**)

Compound **6f** was isolated as a white solid (65% yield): m.p. = 121–123 °C; IR (neat cm^{-1}): 3086 (*v*Ph–H), 2947 (*v*C–H), 1742 (*v*C=O), 1251 (*v*P=O), 1079 (*v*C–O–C), 1054 (*v*P–O–C), 749 (*v*P–C); ^1H NMR (δ/ppm): 3.30 (d, $^3J_{HP}$ = 9.71 Hz, 3H, $-OCH_3$), 3.98 (d, $^2J_{HP}$ = 7.76 Hz 1H, –OCHP), 4.85 (s, 2H, $-OCH_2CO-$), 6.99–7.49 (m, 3H, $-C_6H_3$). Anal. Calc. for $C_{11}H_9Cl_5NaO_6P$: C, 28.21, H, 1.94. Found: C, 27.83, H, 2.08%.

4.5.7. O-Methyl-1-(2,4-dichlorophenoxyacetoxy)-methylphosphonate monopotassium (**6g**)

Compound **6g** was isolated as a white solid (61% yield): m.p. = 162–164 °C; IR (neat cm^{-1}): 3062 (*v*Ph–H), 2958 (*v*C–H), 1740 (*v*C=O), 1234 (*v*P=O), 1072 (*v*C–O–C), 1056 (*v*P–O–C), 736 (*v*P–C); ^1H NMR (δ/ppm): 3.35 (d,$^3J_{HP}$ = 7.28 Hz, 3H, -OCH_3), 4.02 (d, $^2J_{HP}$ = 8.10 Hz, 2H, $-OCH_2P$), 4.91 (s, 2H, $-OCH_2$-CO–), 7.08–7.69 (m, 3H, $-C_6H_3$); MS *m*/*z* (ion, rel. int.): 366 (M^+ 0.39), 234 (0.76), 220 (0.37), 199 (0.68), 175 (1.62), 162 (2.93), 133 (1.47), 127 (1.75), 109 (6.20), 94 (2.36), 93 (2.98), 63 (21.64), 45 (100). Anal. Calc. for $C_{10}H_{10}Cl_2KO_6P$: C, 32.71, H, 2.75. Found: C, 32.42, H, 2.89%.

*4.5.8. O-Methyl-1-(2,4-dichlorophenoxyacetoxy)-ethylphosphonate monopotassium (**6h**)*

Compound **6h** was isolated as a white solid (54% yield): m.p. = 168–170 °C; IR (neat cm^{-1}): 3092 (*v*Ph–H), 2948 (*v*C–H), 1770 (*v*C═O), 1224 (*v*P═O), 1102 (*v*C–O–C), 1046 (*v*P–O–C), 766 (*v*P–C); ^1H NMR (*δ*/ppm): 1.27 (q, $^3J_{HH}$ = 8.00 Hz, 3H, $–CH_3$), 3.38 (d, $^3J_{HP}$ = 9.8 Hz, 3H, $–OCH_3$), 4.83 (s, 2H, $–OCH_2CO–$), 4.99 (d, $^2J_{HP}$ = 9.6 Hz, 1H, –OCHP), 7.06–7.58 (m, 3H, $–C_6H_3$); MS *m*/*z* (ion, rel. int.): 380 (M^+ 0.64), 234 (0.82), 220 (0.67), 199 (0.78), 175 (0.64), 162 (0.93), 133 (1.41), 127 (1.15), 109 (2.20), 94 (1.26), 93 (2.98), 63 (11.44), 45 (100). Anal. Calc. for $C_{11}H_{12}Cl_2KO_6P$: C, 34.66, H, 3.17. Found: C, 34.30, H, 3.16%.

*4.5.9. O-Methyl-1-(2,4-dichlorophenoxyacetoxy)-propylphosphonate monopotassium (**6i**)*

Compound **6i** was isolated as a white solid (52% yield): m.p. = 171–173 °C; IR (neat cm^{-1}): 3048 (*v*Ph–H), 2946 (*v*C–H), 1741 (*v*C═O), 1231 (*v*P═O), 1077 (*v*C–O–C), 1034 (*v*P–O–C), 767 (*v*P–C); ^1H NMR (*δ*/ppm): 0.93 (t, $^3J_{HH}$ = 7.26 Hz, 3H, $–CH_2CH_3$), 1.76–1.86 (m, 2H, $–CH_2CH_3$), 3.56 (d, $^3J_{HP}$ = 9.90 Hz, 3H, $–OCH_3$), 5.03 (s, 2H, $–OCH_2CO–$),5.12 (d, $^2J_{HP}$ = 9.80 Hz 1H, –OCHP), 7.17–7.43 (m, 3H, $–C_6H_3$). MS *m*/*z* (ion, rel. int.): 394 (M^+ 0.21), 234 (0.36), 220 (0.57), 199 (0.67), 175 (1.22), 162 (2.23), 133 (1.23), 127 (0.75), 109 (4.28), 94 (1.36), 93 (3.98), 63 (14.65), 45 (100). Anal. Calc. for $C_{12}H_{14}Cl_2KO_6P$: C, 36.47, H, 3.57. Found: C, 36.29, H, 3.22%.

*4.5.10. O-Methyl-1-(2,4-dichlorophenoxyacetoxy)-butylphosphonate monopotassium (**6j**)*

Compound **6j** was isolated as a white solid (43% yield): m.p. = 146–149 °C; IR (neat cm^{-1}): 3012 (*v*Ph–H), 2960 (*v*C–H), 1728 (*v*C═O), 1230 (*v*P═O), 1077 (*v*C–O–C), 1045 (*v*P–O–C), 718 (*v*P–C); ^1H NMR (*δ*/ppm): 0.83 (t, $^3J_{HH}$ = 4.68 Hz, 3H, $–CH_2CH_2CH_3$), 1.14–1.26 (m, 2H, $–CH_2CH_2CH_3$), 1.67–1.75 (m, 2H, $–CH_2CH_2CH_3$), 3.34 (d, $^3J_{HP}$ = 9.63 Hz, 3H, $–OCH_3$), 4.85(d, $^2J_{HH}$ = 16.44 Hz, $1H^a$, $–OCH_2CO–$), 4.92(d, $^2J_{HH}$ = 16.53 Hz, $1H^b$, $–OCH_2CO–$); 5.00 (d, $^2J_{HP}$ = 14.10 Hz 1H, –OCHP), 7.07–7.60 (m, 3H, $–C_6H_3$); MS *m*/*z* (ion, rel. int.): 408 (M^+ 1.69), 234 (1.69), 220 (2.92), 199 (1.29), 175 (3.53), 162 (1.69), 133 (2.39), 127 (14.69), 109 (3.20), 94 (3.36), 93 (3.48), 63 (8.66), 40 (100). Anal. Calc. for $C_{13}H_{16}Cl_2KO_6P$: C, 38.15, H, 3.94. Found: C, 37.97, H, 3.43%.

Acknowledgments

We gratefully acknowledge financial support of this work by National Key Basic Research Development Program of China (“973” Project No: 2003CB114406) and National Natural Science Foundation of China (Project Nos.: 20072008, 20372023).

References

[1] (a) H.W. He, J. Wang, Z.J. Liu, Chin. Chem. Lett. 5 (1) (1994) 35;
(b) L.M. Hu, H.W. He, Z.J. Liu, Chem. J. Chin. Univ. 17 (12) (1996) 1869;
(c) J. Wang, H.W. He, Z.J. Liu, Chin. Chem. Lett. 8 (11) (1999) 943.
[2] H.W. He, J. Wang, Z.J. Liu, S.Q. Wan, A.h. Lou, Chin. J. Appl. Chem. 11 (6) (1994) 21.
[3] (a) H.W. He, Z.J. Liu, Chin. J. Org. Chem. 21 (11) (2001) 878;
(b) T. Wang, H.W. He, J.L. Yuan, Chin. J. Appl. Chem. 20 (7) (2003) 613.
[4] (a) A.C. Baillie, K. Wright, B.J. Wright, C.G. Earnshaw, Pestic. Biochem. Physiol. 30 (1988) 103;
(b) Petri A. Turhanen, Markku J. Ahlgren, Tomi Jaervinen, Jouko J. Vepsaelaeinen, Synthesis 4 (2001) 633.
[5] H. Mccommbie, B.C. Sauaders, J. Chem. Soc. 38 (1945) 450.
[6] F. Texier-Boullet, A. Foucaud, Synthesis (1982) 165.
[7] F. Texier-Boullet, M. Leouitte, Tetrahedron Lett. 27 (1986) 3515.
[8] P. Coutrot, et al., Synthesis (1986) 661.