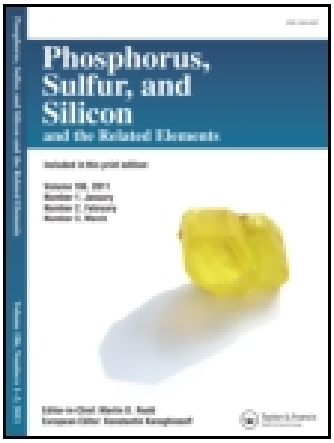

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Synthesis and Herbicidal Activities of Sodium Hydrogen 1-(Substituted Phenoxyacetoxy)Alkylphosphonates

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SYNTHESIS AND HERBICIDAL ACTIVITIES OF SODIUM HYDROGEN 1-(SUBSTITUTED PHENOXYACETOXY)ALKYLPHOSPHONATES

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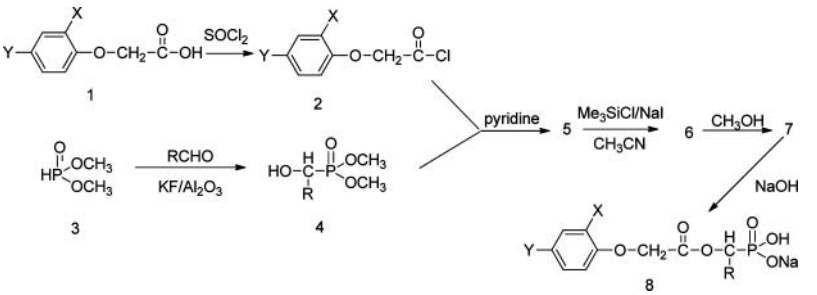
GRAPHICAL ABSTRACT



Abstract *A series of sodium hydrogen 1-(substituted phenoxyacetoxy) alkylphosphonates was designed and synthesized. The test for herbicidal activity indicated that most of the phosphonates (**8**) possessed excellent postemergence herbicidal activities against broadleaf weeds. Especially, **8f** and **8g** showed the best herbicidal activity against rape and amaranth with more than 95% inhibitory rate.*

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.*

Keywords Synthesis; herbicidal activity; phosphonate

INTRODUCTION

Alpha-substituted alkylphosphonate derivatives have received considerable attention in medicine and pesticide chemistry due to their biological activities over the past two

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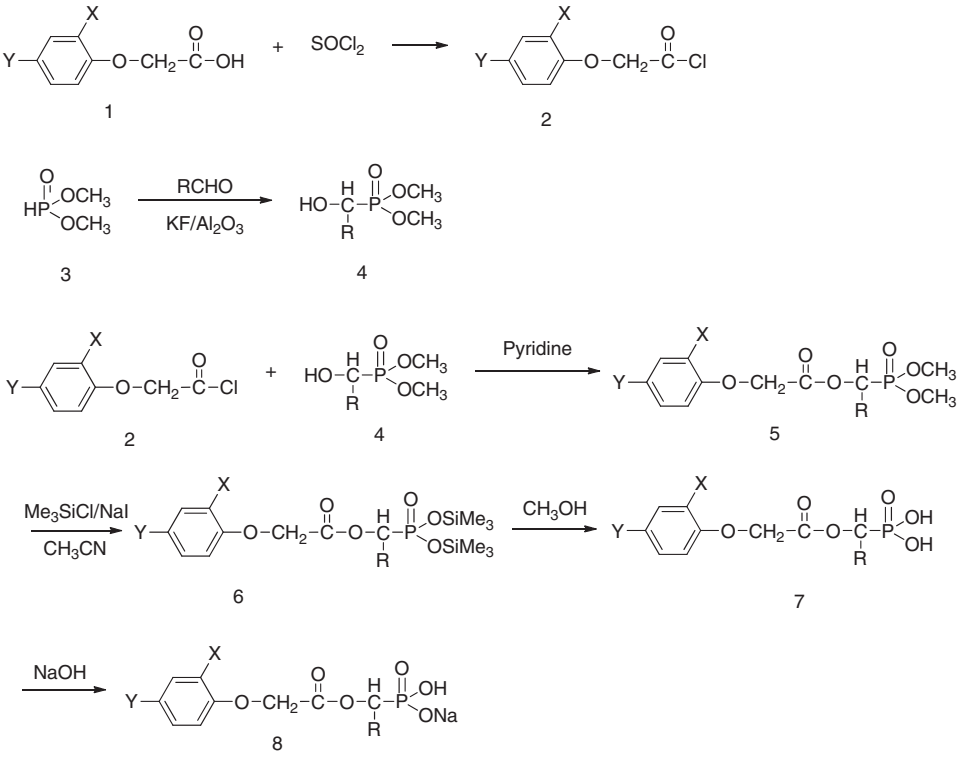
decades.[1–5] Especially, α-(substituted phenoxyacetoxy)alkylphosphonates, as potent pyruvate dehydrogenase complex (PDHc) inhibitors,[6,7] possess notable herbicidal activities.[8] Based on the bioisosterism, their phosphonic acids were assumed to have better herbicidal activity, because phosphonic acid is more analogous to the pyruvic acid, which acts as the substrate of pyruvate dehydrogenase complex.[9] So we are interested in extending our investigations to design some α-(substituted phenoxyacetoxy)alkylphosphonic acids. However, as strong acids, these phosphonic acids themselves would lead the cleavage of carboxylate ester group in the structures.[10] Therefore, monosalts of α-(substituted phenoxyacetoxy)alkylphosphonic acids were designed, which are almost neutral salts with higher stability than the corresponding phosphonic acids. Herein, 13 novel sodium hydrogen 1-(substituted phenoxyacetoxy)alkylphosphonates were synthesized and their herbicidal activities were evaluated.

RESULTS AND DISCUSSION

Syntheses

The multistep procedure for the synthesis of the title phosphonates **8** is outlined in Scheme 1. The methods for the synthesis of substituted phenoxyacetyl chloride



Scheme 1 Synthesis of the title compounds **8**.

2, dimethyl 1-hydroxyalkylalkylphosphonates **4**, and dimethyl 1-(substituted phenoxyacetoxy)alkylphosphonates **5** were adopted, according to the previous work reported in

Table 1 Preparation of sodium hydrogen 1-(substituted phenoxyacetoxy)alkylphosphonates **8a–8m**

Compound	X	Y	R	Appearance	mp (°C)	Yield (%)
8a	Cl	Cl	CH_3	White solid	150–151	88
8b	Cl	Cl	C_2H_5	White solid	133–134	92
8c	Cl	Cl	*n*-C_3H_7	White solid	173–175	86
8d	Cl	Cl	*i*-C_3H_7	White solid	157–158	84
8e	Cl	Cl	*n*-C_4H_9	White solid	179–181	91
8f	Cl	Cl	Phenyl	White solid	145–146	87
8g	Cl	Cl	Thien-2-yl	White solid	135–136	56
8h	CH_3	Cl	CH_3	White solid	140–141	89
8i	CH_3	Cl	C_2H_5	White solid	130–131	89
8j	CH_3	Cl	*n*-C_3H_7	White solid	185–187	83
8k	CH_3	Cl	*i*-C_3H_7	White solid	110–111	93
8l	CH_3	Cl	*n*-C_4H_9	White solid	175–177	87
8m	CH_3	Cl	Phenyl	White solid	108–109	83

our group.[11–13] The phosphonates **5** reacted with chlorotrimethylsilane in acetonitrile using sodium iodide as a catalyst to provide bis(trimethylsilyl) 1-(substituted phenoxyacetoxy)alkylphosphonates 6, which were further transformed into 1-(substituted phenoxyacetoxy)alkylphosphonic acids 7 by reaction with methanol. The title phosphonates 8 were then obtained by the reaction with sodium hydroxide (Table 1).

The structures of the phosphonates **8** were confirmed by **IR**, **^{1}H NMR**, **and** elemental analysis; **8a** and **8h** were also identified via **MS**. The **IR** displayed a weak and wide P-O-H combination peak at 2300–2250 cm^{-1}, P=O stretching vibration at ~1200 cm^{-1}, and the two strong absorption bands at ~1080 cm^{-1}. In the **^{1}H NMR** spectra, the signal of methylene group flanked by the phenoxy and carbonyl appeared as a symmetric quartet, which belongs to the AB coupled system, such as the compound **8f** (Figure S3 in the supplemental material available online).

Herbicidal Activities

The herbicidal activities of the title phosphonates **8** were evaluated at the dosage of 150 g ai/ha in a set of experiments in a greenhouse. They were tested for postemergence inhibitory effect against *Echinochloa crusgalli Beava* (barnyard grass), *Digitaria sanguinalis Scop* (ascendant crabgrass), *Brassica napus L.* (rape), *Amaranthus retroflerus L.* (amaranth), *Setaria viridis* (green bristlegrass) and *Chenopodium serotinum* (small goosefoot). It was found that **8** displayed higher herbicidal activities against dicotyledonous weeds than monocotyledon. The phosphonates **8f** (R = phenyl) and **8g** (R = thien-2-yl) showed the best herbicidal activity against rape and amaranth with more than 95% inhibitory rate. Experimental details and the table of activities (Table S1 and S2) are presented in the supplemental materials available online.

CONCLUSIONS

In conclusion, a series of sodium hydrogen 1-(substituted phenoxyacetoxy) alkylphosphonates were designed and synthesized via the key intermediate 1-(substituted phenoxyacetoxy)alkylphosphonic acids with satisfactory yields. The test for herbicidal

activity indicated that most of the title compounds possessed excellent postemergence herbicidal activities against broadleaf weeds, and they displayed higher herbicidal activities against dicotyledonous weeds than monocotyledon. Especially, sodium hydrogen 1-(2,4-dichlorophenoxyacetoxy)-1-phenylmethylphosphonate and sodium hydrogen 1-(2,4-dichlorophenoxyacetoxy)-1-thien-2'-ylmethylphosphonate showed the best herbicidal activity against rape and amaranth with more than 95% inhibitory rate, which provided some indications for further studies on structure modification.

EXPERIMENTAL

Mass spectra were measured on API2000LC/MS. Infrared spectra were recorded in potassium bromide pellets with a Nicolet Avatar 360 Fourier transform infrared (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded in D_2O solution using sodium 3-(trimethylsilyl)propane-1-sulfonate (DSS) as an internal standard with a Varian Mercury-Plus 400 (400 MHz) spectrometer. Elemental analysis was performed with an Elementar Vario EL III elementary analyzer. Melting points were measured with an electrothermal mp apparatus and are uncorrected.

Synthesis

All of the compounds **1–5** were synthesized (Scheme 1) according to the methods described in the literature.[14–17]

General Procedure for 5

To a solution of dimethyl (1-hydroxyalkyl)phosphonates **4** (10 mmol) and pyridine (14 mmol) in CH_2Cl_2 (25 mL), a solution of substituted phenoxyacetyl chloride **2** (10 mmol) was added dropwise in CH_2Cl_2 (15 mL) at below 5 °C, and the mixture was stirred for 4 h, which was monitored by TLC. The oily residue was purified by flash column chromatography on silica gel with the mixture of acetone/petroleum ether (v:v 1:4) as eluent to furnish **5**.

General Procedure for 6

Under a nitrogen atmosphere and in a dark environment, to a solution of **5** (10 mmol) and sodium iodide (22 mmol) in acetonitrile (25 mL), was added all of trimethylchlorosilane (22 mmol) in one portion at 30 °C, then the reaction mixture was stirred for 2 h. The resultant mixture was purified by flash column chromatography on silica gel with a mixture of petroleum ether/*n*-propanol (v:v 3:1) as eluent to furnish **6** as a colorless oil.

General Procedure for 7

To a solution of **6** (10 mmol) in anhydrous methanol (25 mL), the reaction mixture was stirred for 2–3 h at 30 °C, which was monitored by TLC. The solvent was removed under reduced pressure followed by column chromatography on silica gel with a mixture of petroleum ether/*n*-propanol (v:v 1:3) as eluent to yield **7**.

General Procedure for Compounds (8a–8m)

To a solution of **7** (5.5 mmol) in methanol (20 mL) was added sodium hydroxide (5 mmol) and the mixture was stirred at r.t. for 2 h. Removal of the solvent under reduced pressure, gave the crude product as a white solid, which was recrystallized from acetonitrile to afford **8**.

Sodium hydrogen 1-(2,4-dichlorophenoxyacetoxy)ethylphosphonate (8a). White solid, Yield 88%; **^{1}H NMR** (D_2O) δ: 1.43 (dd, 3H, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 15.0$ Hz, P-CH-C$\underline{H_3}$), 4.93 (s, 2H, O-C$\underline{H_2}$-C), 5.13–5.17 (m, 1H, P-C$\underline{H}$), 7.00 (d, 1H, $^3J_o = 8.8$ Hz, H^6-Ph), 7.30 (dd, 1H, $^3J_o = 8.8$ Hz, $^4J_m = 2.0$ Hz, H^5-Ph), 7.52 (d, 1H, $^4J_m = 2.0$ Hz, H^3-Ph); **ESI-MS**(m/z): positive: 351 (M+1, 12.83%), 259 (21.71%), 107 (100%), 90 (28.58%), 85 (20.97%); negative: 327 (M-23, 100%), 219 (58.74%); **IR** (KBr, ν/cm^{-1}): 3425, 2986, 2938, 1756, 1481, 1439, 1391, 1207, 1083, 921, 871, 802, 720; elemental anal. $C_{10}H_{10}Cl_2NaO_6P$: C, 34.21, H, 2.87; found C, 34.26, H, 2.96.

Sodium hydrogen 1-(2,4-dichlorophenoxyacetoxy)propylphosphonate (8b). White solid, Yield 92%; **^{1}H NMR** (D_2O) δ: 0.91 (t, 3H, $^3J_{HH} = 6.8$ Hz, CH$_2$C$\underline{H_3}$), 1.75–1.95 (m, 2H, C$\underline{H_2}$CH$_3$), 4.93 (s, 2H, O-C$\underline{H_2}$-C), 5.04–5.09 (m, 1H, P-C$\underline{H}$), 7.00 (d, 1H, $^3J_o = 8.8$ Hz, H^6-Ph), 7.29 (dd, 1H, $^3J_o = 8.8$ Hz, $^4J_m = 2.4$ Hz, H^5-Ph), 7.51 (d, 1H, $^4J_m = 2.4$ Hz, H^3-Ph); **IR** (KBr, ν/cm^{-1}): 3419, 2971, 2934, 1747, 1629, 1481, 1436, 1394, 1214, 1082, 936, 893, 799; elemental anal. $C_{11}H_{12}Cl_2NaO_6P$: C, 36.19, H, 3.31; found C, 36.36, H, 3.67.

Sodium hydrogen 1-(2,4-dichlorophenoxyacetoxy)butylphosphonate (8c). White solid, Yield 86%; **^{1}H NMR** (D_2O) δ: 0.87 (t, 3H, $^3J_{HH} = 6.8$ Hz, CH$_2$C$\underline{H_3}$), 1.21–1.41 (m, 2H, C$\underline{H_2}$CH$_3$), 1.75–1.80 (m, 2H, P-CH-C$\underline{H_2}$), 4.97 (s, 2H, O-C$\underline{H_2}$-C), 5.14–5.20 (m, 1H, P-C$\underline{H}$), 7.00 (d, 1H, $^3J_o = 8.8$ Hz, H^6-Ph), 7.30 (dd, 1H, $^3J_o = 8.8$ Hz, $^4J_m = 2.4$ Hz, H^5-Ph), 7.53 (d, 1H, $^4J_m = 2.4$ Hz, H^3-Ph); **IR** (KBr, ν/cm^{-1}): 3431, 2962, 2933, 2874, 2314, 1748, 1650, 1481, 1436, 1393, 1290, 1206, 1082, 917, 871, 802, 720; elemental anal. $C_{12}H_{14}Cl_2NaO_6P$: C, 38.02, H, 3.72; found C, 37.90, H, 4.18.

Sodium hydrogen 1-(2,4-dichlorophenoxyacetoxy)-2-methylpropylphosphonate (8d). White solid, Yield 84%; **^{1}H NMR** (D_2O) δ: 0.97 (t, 6H, $^3J_{HH} = 6.8$ Hz, $^4J_{PH} = 6.8$ Hz, P-CH-CH(C$\underline{H_3}$)$_2$), 2.15–2.22 (m, 1H, P-CH-C$\underline{H}$), 4.95–5.05 (m, 2H, O-C$\underline{H_2}$-C; 1H, P-C$\underline{H}$), 7.00 (d, 1H, $^3J_o = 8.8$ Hz, H^6-Ph), 7.30 (dd, 1H, $^3J_o = 8.8$ Hz, $^4J_m = 2.4$ Hz, H^5-Ph), 7.52 (d, 1H, $^4J_m = 2.4$ Hz, H^3-Ph); **IR** (KBr, ν/cm^{-1}): 3419, 2966, 2933, 2354, 1747, 1650, 1480, 1438, 1391, 1291, 1215, 1079, 1049, 921, 870, 801, 718; elemental anal. $C_{12}H_{14}Cl_2NaO_6P$: C, 38.02, H, 3.72; found C, 38.10, H, 3.49.

Sodium hydrogen 1-(2,4-dichlorophenoxyacetoxy)pentylphosphonate (8e). White solid, Yield 91%; **^{1}H NMR** (D_2O) δ: 0.89 (t, 3H, $^3J_{HH} = 6.8$ Hz, CH$_2$C$\underline{H_3}$), 1.23–1.27 (m, 4H, C$\underline{H_2}$C$\underline{H_2}$), 1.75–1.80 (m, 2H, P-CH-C$\underline{H_2}$), 4.98 (s, 2H, O-C$\underline{H_2}$-C), 5.13–5.17 (m, 1H, P-C$\underline{H}$), 7.01 (d, 1H, $^3J_o = 8.8$Hz, H^6-Ph), 7.31 (d, 1H, $^3J_o = 8.8$ Hz, H^5-Ph), 7.54 (s, 1H, H^3-Ph); **IR** (KBr, ν/cm^{-1}): 3430, 2958, 2931, 1749, 1482, 1436, 1392, 1290, 1216, 1079, 923, 869, 801, 719; elemental anal. $C_{13}H_{16}Cl_2NaO_6P$: C, 39.72, H, 4.10; found C, 39.67, H, 4.05.

Sodium hydrogen 1-(2,4-dichlorophenoxyacetoxy)-1-phenylmethylphosphonate (8f). White solid, Yield 87%; **^{1}H NMR** (D_2O) δ: 5.00, 5.02 (q, AB system, 2H, $^2J_{AB} = 16.4$ Hz, O-C$\underline{H_2}$-C), 5.89 (d, 1H, $^3J_{PH} = 12.4$ Hz, P-C$\underline{H}$), 6.85 (d, 1H, $^3J_o = 8.8$ Hz, H^6-Ph-O), 7.17 (dd, 1H, $^3J_o = 8.8$ Hz, $^4J_m = 2.4$ Hz, H^5-Ph-O), 7.33–7.44 (m, 5H, C$_6$H$_5$-CH), 7.47 (d, 1H, $^4J_m = 2.4$ Hz, H^3-Ph-O); **IR** (KBr, ν/cm^{-1}): 3420, 2930, 1747, 1634, 1480,

1453, 1394, 1218, 1081, 912, 871, 802, 720; elemental anal. $C_{15}H_{12}Cl_2NaO_6P$: C, 43.61, H, 2.93; found C, 43.97, H, 3.17.

Sodium hydrogen 1-(2,4-dichlorophenoxyacetoxy)-1-thien-2'-ylmethylphosphonate (8g). White solid, Yield 56%; **^{1}H NMR** (D_2O) δ: 4.94 (m, 2H, O-CH_2-C), 6.30 (d, 1H, $^3J_{PH}$ = 12.4 Hz, P-CH), 6.75–6.80 (m, 1H, H^6-Ph-O; 1H, 3-thienyl-H), 7.03–7.22 (m, 1H, H^5-Ph-O; 1H, 4-thienyl-H), 7.36–7.44 (m, 1H, H^3-Ph-O; 5-thienyl-H); **IR** (KBr, ν/cm^{-1}): 3417, 3103, 2929, 1757, 1625, 1480, 1434, 1392, 1196, 1080, 912, 802, 707; elemental anal. $C_{13}H_{10}Cl_2NaO_6PS$: C, 37.25, H, 2.40, S, 7.65; found C 37.12, H, 2.32, S, 7.78.

Sodium hydrogen 1-(4-chloro-2-methylphenoxyacetoxy)ethylphosphonate (8h). White solid, Yield 89%; **^{1}H NMR** (D_2O) δ: 1.42 (dd, 3H, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 15.2 Hz, P-CH-C$\underline{H}_3$), 2.24 (s, 3H, C_6H_3-C$\underline{H}_3$), 4.86 (s, 2H, O-CH_2-C), 5.13–5.16 (m, 1H, P-CH), 6.84 (d, 1H, ^3J_o = 8.8 Hz, H^6-Ph), 7.18 (t, 1H, ^3J_o = 8.8 Hz, H^5-Ph), 7.26 (s, 1H, H^3-Ph); **IR** (KBr, ν/cm^{-1}): 3423, 2958, 1759, 1634, 1493, 1444, 1380, 1219, 1186, 1138, 1074, 997, 919, 876, 800; **ESI-MS**(m/z): positive: 353(M+23, 100%), 330(M^+, 7.91%), 301(77.68%), 250(11.64%), 245(20.43%), 136(4.03%); negative: 309(M-23+2, 31.31%), 307(M-23, 100%), 199(8.10%), 165(3.47%), 141(6.34%), 125(28.92%), 107(68.95%), 63(66.92%); elemental anal. $C_{11}H_{13}ClNaO_6P$: C, 39.96, H, 3.96; found: C, 39.78, H, 3.87.

Sodium hydrogen 1-(4-chloro-2-methylphenoxyacetoxy)propylphosphonate (8i). White solid, Yield 89%; **^{1}H NMR** (D_2O) δ: 0.91 (t, 3H, $^3J_{HH}$ = 6.8 Hz, $CH_2C\underline{H}_3$), 1.75–1.89 (m, 2H, $C\underline{H}_2CH_3$), 2.24 (s, 3H, C_6H_3-C$\underline{H}_3$), 4.90 (s, 2H, O-CH_2-C), 5.05–5.10 (m, 1H, P-CH), 6.85 (d, 1H, ^3J_o = 8.8 Hz, H^6-Ph), 7.18 (d, 1H, ^3J_o = 8.8 Hz, H^5-Ph), 7.26 (s, 1H, H^3-Ph); **IR** (KBr, ν/cm^{-1}): 3422, 2973, 2934, 2878, 2361, 1748, 1651, 1492, 1438, 1383, 1216, 1186, 1072, 941, 800; elemental anal. $C_{12}H_{15}ClNaO_6P$: C, 41.82, H, 4.39; found C, 41.69, H, 4.31.

Sodium hydrogen 1-(4-chloro-2-methylphenoxyacetoxy)butylphosphonate (8j). White solid, Yield 83%; **^{1}H NMR** (D_2O) δ: 0.85 (t, 3H, $^3J_{HH}$ = 6.8 Hz, $CH_2C\underline{H}_3$), 1.18–1.33 (m, 2H, $C\underline{H}_2CH_3$), 1.77–1.81 (m, 2H, P-CH-C$\underline{H}_2$), 2.15 (s, 3H, C_6H_3-C$\underline{H}_3$), 4.68–4.82 (m, 2H, O-CH_2-C), 5.15–5.20 (m, 1H, P-CH), 6.68 (d, 1H, ^3J_o = 8.8 Hz, H^6-Ph), 7.03 (d, 1H, ^3J_o = 8.8 Hz, H^5-Ph), 7.05 (s, 1H, H^3-Ph); **IR** (KBr, ν/cm^{-1}): 3419, 2962, 2874, 2315, 1742, 1634, 1492, 1294, 1223, 1187, 1138, 1070, 912, 801; elemental anal. $C_{13}H_{17}ClNaO_6P$: C, 43.53, H, 4.78; found: C, 43.26, H, 4.72.

Sodium hydrogen 1-(4-chloro-2-methylphenoxyacetoxy)-2-methylpropyl phosphornate (8k). White solid, Yield 93%; **^{1}H NMR** (D_2O) δ: 0.97 (t, 6H, $^3J_{HH}$ = 6.8 Hz, CH(C$\underline{H}_3$)$_2$), 2.20–2.24 (m, 1H, P-CH-C$\underline{H}$), 2.24 (s, 3H, C_6H_3-C$\underline{H}_3$), 4.91–5.00 (m, 2H, O-CH_2-C; 1H, P-CH), 6.84 (d, 1H, ^3J_o = 8.4 Hz, H^6-Ph), 7.19 (d, 1H, ^3J_o = 8.4 Hz, H^5-Ph), 7.25 (s, 1H, H^3-Ph); **IR** (KBr, ν/cm^{-1}): 3421, 2965, 2931, 2327, 1748, 1651, 1493, 1386, 1300, 1218, 1187, 1138, 1071, 920, 800; elemental anal. $C_{13}H_{17}ClNaO_6P$: C, 43.53, H, 4.78; found C, 43.32, H, 4.65.

Sodium hydrogen 1-(4-chloro-2-methylphenoxyacetoxy)pentylphosphonate (8l). White solid, Yield 87%; **^{1}H NMR** (D_2O) δ: 0.83 (t, 3H, $^3J_{HH}$ = 6.4 Hz, $CH_2C\underline{H}_3$), 1.18–1.28 (m, 4H, $C\underline{H}_2C\underline{H}_2$), 1.75–1.80 (m, 2H, P-CH-C$\underline{H}_2$), 2.24 (s, 3H, C_6H_3-C$\underline{H}_3$), 4.90 (s, 2H, O-CH_2-C), 5.11–5.16 (m, 1H, P-CH), 6.85 (d, 1H, ^3J_o = 8.8 Hz, H^6-Ph), 7.19 (d, 1H, ^3J_o = 8.8 Hz, H^5-Ph), 7.26 (s, 1H, H^3-Ph); **IR** (KBr, ν/cm^{-1}): 3424, 2958, 2930, 2322, 1734, 1651, 1492, 1438, 1383, 1297, 1220, 1187, 1137, 1069, 923, 874, 800; elemental anal. $C_{14}H_{19}ClNaO_6P$: C, 45.12, H, 5.14; found C, 44.78, H, 5.11.

Sodium hydrogen 1-(4-chloro-2-methylphenoxyacetoxy)-1-phenylmethyl phosphonate (8m). White solid, Yield 83%; **^{1}H NMR** (D_2O) δ: 2.04 (s, 3H, C_6H_3-C$\underline{H}_3$),

4.71–4.74 (m, 2H, O-CH_2-C), 5.99 (d, 1H, $^3J_{PH} = 12.8$ Hz, P-CH), 6.47 (s, 1H, H^6-Ph-O), 6.85 (s, 1H, H^5-Ph-O), 6.97 (s, 1H, H^3-Ph-O), 7.30–7.38 (m, 5H, $C_6\underline{H}_5$-CH); **IR** (KBr, ν/cm^{-1}): 3432, 2927, 1748, 1635, 1492, 1454, 1186, 1137, 1073, 927, 881, 801; elemental anal. $C_{16}H_{15}ClNaO_6P$: C, 48.94, H, 3.85; found C, 48.67, H, 3.67.

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