Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Fluorine Chemistry 127 (2006) 291–295
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Short communication

Synthesis and herbicidal activity of *O*,*O*-dialkyl phenoxyacetoxyalkylphosphonates containing fluorine

Ting Chen, Ping Shen, Yanjun Li, Hongwu He *

Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

Received 13 August 2005; received in revised form 4 November 2005; accepted 11 November 2005

Abstract

A series of substituted phenoxyacetoxyalkylphosphonates bearing fluorine were designed and synthesized. All the new compounds were identified by elemental analysis, IR, ^{1}H NMR and MS and were tested for herbicidal activity in greenhouse at a rate of 1.5 kg/ha. The results of preliminary bioassay showed that fluorine moiety introduced to the core structure could help to improve the herbicidal activity, and compounds with a 3-trifluoromethyl in benzene ring exhibited higher inhibitory activity.

Keywords: Fluorophenoxyacetic acid; 1-Hydroxyl alkylphosphonates; Synthesis; Herbicidal activity

1. Introduction

Fluorine is a very unique element with the highest electronegativity, smallest size next to hydrogen, high thermal stability and lipophilicity, which endows various prominent functionality in the organofluorine compounds. By introducing fluorine atom into organic molecules, we can get compounds with improved physical, chemical and biological properties [1–3]. So, the application of fluorides in pharmaceuticals and pesticides attracted more and more attention. Some examples demonstrated that fluorine-introducing could influence the herbicidal activity [4], fungicidal activity [5] and insecticidal activity [6] of certain compounds.

How to find effective herbicides with novel structures and mode of action has become a new focus of pesticide discovery. For a long time, our group was actively engaged in the research of bioactive organophosphonates. Recent study revealed that 1-oxophosphonic acid derivatives, which possessed good herbicidal activities, could act as a leading structure for herbicide designing [7]. However, our previous work was devoted to neither the synthesis of fluorosubstituted phenoxyacetoxyalkylphosphonates, nor the systematic structure–activity study of this kind of compound. This ideal encouraged us to introduce fluorine moiety to the core structure as a continuous research of our previous work. Here, we report our recent study about the synthesis and herbicidal activity of a novel series of *O*,*O*-dialkyl 1-(fluorosubstituted) phenoxyacetoxyalkylphosphonates (**5a**–**5l**).

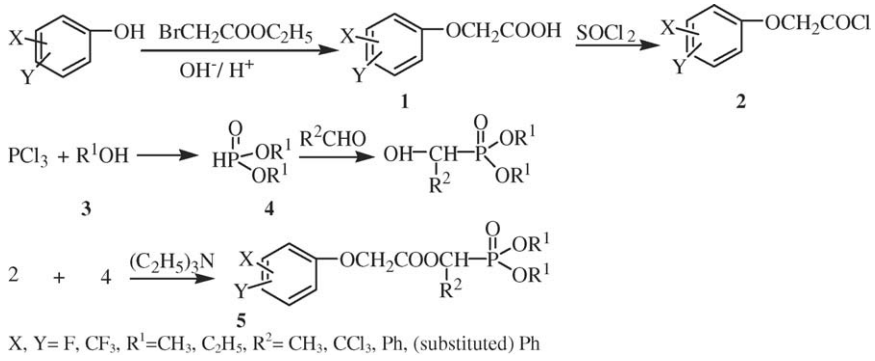
2. Results and discussions

2.1. Synthesis

Compound **1** could be easily synthesized starting from fluorophenol and bromoacetic ester [8]. Dimethyl phosphite and diethyl phosphite **3** were obtained by the reported method [9]. The preparation of title compounds involved the condensation of fluorophenoxyacetyl chloride moiety **2** and *O*,*O*-dialkyl 1-hydroxylalkylphosphonates moiety **4**. As the target phosphonate derivatives containing groups sensitive to acid, base or water, such as carboxylic ester, so the reaction required a temperature near room temperature and the reagent in anhydrous solvents. The synthetic pathway was outlined in Scheme 1 and the structures of title compounds **5a**–**5l** were given in Table 1.

* Corresponding author. Tel.: +86 27 67867960; fax: +86 27 67867960.
E-mail addresses: he1208@public.wh.hb.cn, he1208@mail.ccnu.edu.cn (H.W. He).

0022-1139/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2005.11.013



Scheme 1.

2.2. Biological activities

The herbicidal activities of compounds **5a–5l** were evaluated at a rate of 1.5 a.i. kg/ha in a set of experiment in greenhouse. They were tested for pre-emergence and post-emergence inhibitory effect against *Echinochloa Crusgalli Beava* (barngard grass), *Digitaria Sanguinalis scop* (ascendant crabgrass), *Brassica napus* L. (rape), *Amaranthus retroflerus* L. (amaranth) and *Medicago Satival* (clover).

Plastic pots were packed with sandy clay loam soil and water was added up to 3 cm in depth. About 15–20 seeds of plants were sown in the soil at a depth of 5 mm and grown at 20–25 °C for a few days. The diluted solution of each compound containing acetone and Tween 80 were applied into the pots at 1.5 a.i. kg/ha. Twenty days later, the pre-emergence herbicidal activity was visually evaluated. At the post-emergence, the solution was applied to the foliage of plants grown at two to three leaves stage with a sprayer at the rate of 1.5 a.i. kg/ha with a spelling volume of 1000 L/ha. All the treatments were replicated three times in a completely randomized design. The test plants were harvested 20 days after sowing, and determined for fresh weight. The post-emergence herbicidal activity against each weed was evaluated. The percentage growth inhibition of roots and aerial parts were calculated in relation to the mass of the roots and aerial parts of the control respectively. The results of **5a–5l** were listed in Table 1.

As seen from Table 1, compounds **5a–5d** showed much better activity than that of compounds **5e**, **5f**, **5g**, **5h**, **5k**, **5l**. Compounds **5a–5d** exhibited notable pre-emergence inhibitory effects against a variety of plants species, specially **5a**, **5b**, **5d** showed good pre-emergence and post-emergence inhibitory effects against dicotyledon. Such as *Amaranthus retroflerus* L. and *Medicago Satival*.

Compounds **5m–5n** [10] and **5o–5t** [11–13] also listed in Table 1 were employed to discuss about the bioactivity. They were obtained from our previous work.

Table 1
Herbicidal activity of compounds **5a–5t** (1.5 a.i. kg/ha, relative inhibition of growth percent)

Compound	X	Y	R^1	R^2	Ech.		Dig.		Bra.		Ama.		Med.	
					Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
5a	H	3-CF_3	CH_3	3-ClPh	62.8	37.5	87.2	0	22.1	59.6	100	92.3	93.2	100
5b	H	3-CF_3	C_2H_5	3-ClPh	73.5	0	72.3	8.0	51.6	37.6	95.5	84.5	96.6	88.3
5c	H	3-CF_3	CH_3	4-FPh	68.5	16.0	86.6	16.0	82.7	35.2	67.7	57.6	89.7	100
5d	H	3-CF_3	C_2H_5	4-FPh	35.5	8.3	100	32.0	50.4	49.6	77.3	88.5	100	100
5e	H	2-F	CH_3	Ph	0	27.3	0	18.2	0	0	0	0	0	0
5f	H	2-F	CH_3	3-NO_2Ph	0	80.3	0	33.9	0	17.3	0	0	0	0
5g	H	3-F	CH_3	Ph	0	0	0	10.4	0	3.0	0	48.6	0	0
5h	H	3-F	CH_3	3-NO_2Ph	0	19.4	5.4	0	0	0	0	6.8	0	0
5i	2-F	4-F	CH_3	CH_3	36.0	20.2	73.6	48.5	39.3	61.0	38.9	77.5	52.1	49.4
5j	2-F	4-F	CH_3	CCl_3	11.8	21.6	64.3	46.2	17.6	41.2	25.0	71.1	64.6	49.4
5k	3-F	5-F	CH_3	CH_3	0	3.8	0	27.2	0	0	0	14.9	10.4	0
5l	3-F	5-F	CH_3	CCl_3	8.1	22.5	0	12.6	6.2	15.2	0	39.0	0	0
5m [10]	2-Cl	3-Cl	CH_3	CH_3	19.1	13.6	0	35.0	0	23.3	16.7	43.8	8.3	0
5n [10]	2-Cl	3-Cl	CH_3	CCl_3	5.1	6.1	0	22.7	24.1	0	0	37.3	20.8	0
5o [11]	H	4-CH_3	CH_3	CH_3	\	47.4	0	0	62.17	30.9	\	0	\	\
5p [12]	H	2-NO_2	CH_3	3-NO_2Ph	2.3	0	6.7	0.3	0.9	0	\	\	\	\
5q [12]	H	4-NO_2	CH_3	Ph	0.8	0	0	−5.2	−2.78	5.49	\	\	\	\
5r [12]	H	4-NO_2	CH_3	3-NO_2Ph	−1.1	−2.5	5.26	0.3	−16.7	−1.1	\	\	\	\
5s [13]	H	3-CF_3	C_2H_5	Ph	90.2	51.4	100	16.0	43.3	83.7	91.0	84.6	100	100
5t [13]	H	3-CF_3	C_2H_5	3-NO_2Ph	88.3	0	97.9	32.0	33.9	61.7	100	84.6	100	83.3

Post, post-emergence treatment; pre, pre-emergence treatment; Ech., *Echinochloa crusgalli Beava*; Dig., *Digitaria sanguinalis Scop*; Bra., *Brassica napus* L.; Ama., *Amaranthus retroflerus* L.; Med., *Medicago sativa*; rate of compound **5o** was 2.25 kg/ha; \, the data for the activity was not tested.

The results indicated that fluorine moiety introduced to *O*,*O*-dialkyl 1-(substituted) phenoxyacetoxyalkylphosphonate's structure was useful for the improvement of herbicidal activity. Especially, the introducing of trifluoromethyl group made for prominent enhancement on inhibitory activity.

From the table, we noticed that the structure and position of substituents X, Y in benzene ring had great influence on the herbicidal activity. For monosubstituted benzene ring, trifluoromethyl substituted compounds have the best activity. For disubstituted benzene ring, the combination of 2-F, 4-F was better than that of 3-F, 5-F and 2-Cl, 3-Cl. Comparing compounds **5i**–**5l** with **5e**–**5h**, obvious increasement of inhibitory activity was observed by introducing two fluorine atoms. Whereas the change of other substituents, such as R^1 or R^2, has only a little influence on their activity. Further exploring of structure–activity relationship need more experimental results to support. In our group, the QSAR studies of substituted phenoxyacetoxyalkylphosphonates, including the title compounds, are in process.

As a conclusion, the herbicidal activity of the title compounds could be improved to some extent by introducing fluorine moiety to benzene ring. However, it needed reasonable combination of the structure and position of substituents at the benzene ring. These results provided some interesting hints for further study of structure modification and structure–activity relationship of this kind of compounds.

3. Experimental

Mass spectra were measured on a Finnigan TraceMS 2000 spectrometer. Infrared spectra were recorded in potassium bromide disks on a Nicolet Avatar360 FTIR spectrometer. ^{1}H NMR was recorded in deuterocholroform solution at 400 MHz, using tetramethysilane as internal standard on Varian Mercury-Plus400 spectrometer. Elemental analysis was performed by Elementar Vario EL III elementary analyzer. Melting points (mp) were measured on an electrothermal melting point apparatus and temperature uncorrected. All the solvents were dried before use. Phosphorous trichloride, triethyl amine and thionyl chloride were distilled before the reaction. Samples were purified by flash chromatography with silica gel.

*3.1. Synthesis of fluorophenoxyacetic acid (**1**) and fluorophenoxyacetyl chloride (**2**)*

To a three-neck boiling flask, fluorophenol (0.04 mol), bromoacetic ester (0.042 mol), potassium carbonate (5.8 g) were added by order, then Me_2SO (100 mL) was added as solvent. The mixture was stirred and kept at 70–80 °C for 5 h, then was treated with ice-water immediately. After the yellow solid was filtered off, and dissolved in acetone (20 mL), 2 mol/L NaOH was added, then stirred for another 2 h at room temperature. Then added 2 mol/L HCl and the fluorophenoxyacetic acid **1** formed. The solid could be recrystalized as white crystal in yield of 70%. The corresponding fluorophenoxyacetyl chloride **2** could be easily obtained as a yellow liquid in 90% yield by treated compound **1** with thionyl chloride.

*3.2. Synthesis of O,O-dialkyl 1-hydroxylalkphosphonate (**4**)*

O,*O*-Dimethyl 1-hydroxyalkylphosphonate or *O*,*O*-diethyl 1-hydroxyalkylphosphonate **4** could be prepared by the reaction of dimethyl phosphite or diethyl phosphite **3** and several kinds of aldehydes using potassium fluoride and alumina (mass ratio was 1:1) as catalyst in yield of 65–94% according to literatures [14,15].

*3.3. General synthesis of fluorophenoxyacetoxyalkylphosphonates (**5a**–**5l**)*

A solution of fluorophenoxyacetyl chloride **2** (0.011 mol) in trichloromethane (15 mL) was added to stirred mixture of 1-hydroxy alkylphosphonate **4** (0.01 mol) and triethyl amine (0.011 mol) in trichloromethane (15 mL) at 2–4 °C. The resultant mixture was stirred at ambient temperature for 2–3 h, then washed with 0.1 mol/L HCl, saturated $NaHCO_3$ and brine separately, dried and evaporated. The residue was chromatographed on silica with 20% acetone in petroleum ether as eluent to give the compounds **5a**–**5l** as a yellow liquid or white solid.

*3.3.1. O,O-Dimethyl 1-(3-trifluoromethylphenoxyacetoxy)3-chlorobenzylphosphonate (**5a**)*

Oil: yield 70.1%; n_D^{20} 1.5138; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 3.65–3.79 (m, 6H, $2OCH_3$), 4.75 (s, 2H, OCH_2CO), 6.18–6.20 (d, 1H, OCHP, J_{HP} = 13.3 Hz), 7.04–7.47 (m, 8H, $2C_6H_4$); IR (KBr) (cm^{-1}): 3076 (Ar–H), 1753 (C=O), 1265 (P=O), 742 (P–C); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 452 $[M]^+$ (17.49), 175 (98.3), 109 (70.87), 93 (100); anal. calc. for $C_{18}H_{17}O_6PF_3Cl$: C, 47.73, H, 3.76. Found: C, 47.85, H, 3.70%.

*3.3.2. O,O-Diethyl 1-(3-trifluoromethylphenoxyacetoxy)3-chlorobenzylphosphonate (**5b**)*

Crystal: yield 63.7%; mp 36.4–36.8 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 1.25–1.30 (m, 6H, $2OCH_2CH_3$), 3.82–4.20 (m, 4H, $2OCH_2CH_3$), 4.77 (s, 2H, OCH_2CO), 6.18–6.20 (d, 1H, OCHP, J_{HP} = 13.3 Hz), 7.03–7.47 (m, 8H, $2C_6H_4$); IR (KBr) (cm^{-1}): 3070 (Ar–H), 1750 (C=O), 1263 (P=O), 742 (P–C); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 480 $[M]^+$ (27.91), 175 (94.21), 121(100), 93 (84.43); anal. calc. for $C_{20}H_{21}O_6PF_3Cl$: C, 49.95, H, 4.37. Found: C, 50.10, H, 4.42%.

*3.3.3. O,O-Dimethyl 1-(3-trifluoromethylphenoxyacetoxy)4-fluorobenzylphosphonate (**5c**)*

Crystal: yield 79.2%; mp 69.3–69.5 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 3.62–3.79 (m, 6H, $2OCH_3$), 4.77 (s, 2H, OCH_2CO), 6.61–6.67 (d, 1H, OCHP, J_{HP} = 13.3 Hz), 7.04–7.34 (m, 8H, $2C_6H_4$); IR (KBr) (cm^{-1}): 3070 (Ar–H), 1748 (C=O), 1263 (P=O), 742 (P–C); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 436 $[M]^+$ (1.06), 175 (97.13), 145 (100), 93 (17.99); anal. calc. for $C_{18}H_{17}O_6PF_4$: C, 49.54, H, 3.90. Found: C, 49.00, H, 3.57%.

*3.3.4. O,O-Diethyl 1-(3-trifluoromethylphenoxyacetoxy)4-fluorobenzylphosphonate (**5d**)*

Oil: yield 70.1%; n_D^{20} 1.4945; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 1.20–1.30 (m, 6H, $2OCH_2CH_3$), 3.90–4.20 (m, 4H, $2OCH_2CH_3$), 4.79 (s, 2H, OCH_2CO), 6.30–6.38 (d, 1H, OCHP, J_{HP} = 13.3 Hz), 7.03–7.47 (m, 8H, $2C_6H_4$); IR (KBr) (cm^{-1}): 3069 (Ar–H), 1747 (C=O), 1263 (P=O), 744 (P–C); EIMS (probe) 70 eV, *m/z* (rel. int.): 465 $[M]^+$ (6.13), 175 (79.02), 121(100); anal. calc. for $C_{20}H_{21}O_6PF_4$: C, 51.72, H, 4.53. Found: C, 51.72, H, 4.69%.

*3.3.5. O,O-Dimethyl 1-(2-fluorophenoxyacetoxy)benzylphosphonate (**5e**)*

Crystal: yield 64.0%; mp 67.2–67.8 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 3.62–3.72 (m, 6H, $2OCH_3$), 4.83 (s, 2H, OCH_2CO), 6.25–6.28 (d, 1H, OCHP, J_{HP} = 13.2 Hz), 7.04–7.46 (m, 8H, C_6H_4, C_6H_5); IR (KBr) (cm^{-1}): 3056 (Ar–H), 1747 (C=O), 1269 (P=O), 740 (P–C); EIMS (probe) 70 eV, *m/z* (rel. int.): 368 $[M]^+$(21.56), 109 (28.20), 93 (100); anal. calc. for $C_{17}H_{18}O_6PF$: C, 55.44, H, 4.93. Found: C, 55.56, H, 4.76%.

*3.3.6. O,O-Dimethyl 1-(2-fluorophenoxyacetoxy)3-nitrobenzylphosphonate (**5f**)*

Crystal: yield 72.9%; mp 82.7–83.6 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 3.81–3.72 (m, 6H, $2OCH_3$), 4.88 (s, 2H, OCH_2CO), 6.31–6.34 (d, 1H, OCHP, J_{HP} = 13.2 Hz), 6.93–8.29 (m, 8H, $2C_6H_4$); IR (KBr) (cm^{-1}): 3078 (Ar–H), 1740 (C=O), 1260 (P=O), 741 (P–C) EIMS (probe) 70 eV, *m/z* (rel. int.): 413 $[M]^+$ (13.09), 125 (99.27), 109 (77.36), 93 (100); anal. calc. for $C_{17}H_{17}O_8PFN$: C, 49.40, H, 4.15, N, 3.39. Found: C, 49.77, H, 3.98, N, 3.34%.

*3.3.7. O,O-Dimethyl 1-(3-fluorophenoxyacetoxy)benzylphosphonate (**5g**)*

Crystal: yield 65.9%; mp 48.7–49.5 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 3.63–3.72 (m, 6H, $2OCH_3$), 4.70 (s, 2H, OCH_2CO), 6.31–6.36 (d, 1H, OCHP, J_{HP} = 13.3 Hz), 6.61–7.47 (m, 8H, C_6H_4, C_6H_5); IR (KBr) (cm^{-1}): 3069 (Ar–H), 1744 (C=O), 1269 (P=O), 741 (P–C); EIMS (probe) 70 eV, *m/z* (rel. int.): 368 $[M]^+$ (49.97), 125 (66.36), 109 (75.18), 95 (100); anal. calc. for $C_{17}H_{18}O_6PF$: C, 55.40, H, 4.93. Found: C, 55.94, H, 4.65%.

*3.3.8. O,O-Dimethyl 1-(3-fluorophenoxyacetoxy)3-nitrobenzylphosphonate (**5h**)*

Crystal: yield 61.5%; mp 83.8–84.2 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 3.73–3.82 (m, 6H, $2OCH_3$), 4.81 (s, 2H, OCH_2CO), 6.32–6.35 (d, 1H, OCHP, J_{HP} = 13.2 Hz), 6.93–8.30 (m, 8H, $2C_6H_4$); IR (KBr) (cm^{-1}): 3056 (Ar–H), 1748 (C=O), 1256 (P=O), 743 (P–C); EIMS (probe) 70 eV, *m/z* (rel. int.): 413 $[M]^+$ (0.15), 125 (100), 109 (84.99), 93 (90.26); anal. calc. for $C_{17}H_{17}O_8PFN$: C, 49.40, H, 4.15, N, 3.39. Found: C, 49.98, H, 4.05, N, 3.22%.

*3.3.9. O,O-Dimethyl 1-(2,4-difluorophenoxyacetoxy)ethylphosphonate (**5i**)*

Crystal: yield 68.3%; mp 38.4–40.1 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 1.48–1.54 (d, 3H, CH_3), 3.77–3.82 (m, 6H, $2OCH_3$), 4.72 (s, 2H, OCH_2CO), 5.31–5.47 (m, 1H, OCHP, J_{HP} = 13.3 Hz), 6.79–7.96 (m, 3H, C_6H_3); IR (KBr) (cm^{-1}): 3069 (Ar–H), 1744(C=O), 1262 (P=O), 740 (P–C); EIMS (probe) 70 eV, *m/z* (rel. int.): 324 $[M]^+$ (80.71), 138 (100), 109 (92.21), 93 (83.78); anal. calc. for $C_{12}H_{15}O_6PF_2$: C, 44.46, H, 4.66. Found: C, 44.73, H, 4.45%.

*3.3.10. O,O-Dimethyl 1-(2,4-difluorophenoxyacetoxy)trichloromethylmethylphosphonate (**5j**)*

Crystal: yield 65.2%; mp 67.9–68.5 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 3.81–3.93 (m, 6H, $2OCH_3$), 4.66 (s, 2H, OCH_2CO), 5.96–5.97 (d, 1H, OCHP, J_{HP} = 13.3 Hz), 6.79–7.28 (m, 3H, C_6H_3); IR (KBr) (cm^{-1}): 3078 (Ar–H), 1744 (C=O), 1263 (P=O), 744 (P–C); EIMS (probe) 70 eV, *m/z* (rel. int.): 426 $[M]^+$ (44.23), 205 (79.71), 109 (99.59), 93 (100); anal. calc. for $C_{12}H_{12}Cl_3O_6PF_2$: C, 33.71, H, 2.83. Found: C, 33.54, H, 2.62%.

*3.3.11. O,O-Dimethyl 1-(3,5-difluorophenoxyacetoxy)ethylphosphonate (**5k**)*

Oil: yield 57.2%; n_D^{20} 1.4721; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 1.50–1.56 (d, 3H, CH_3), 3.77–3.82 (m, 6H, $2OCH_3$), 4.68 (s, 2H, OCH_2CO), 5.40–5.44 (m, 1H, OCHP, J_{HP} = 13.2 Hz), 6.42–7.48 (m, 3H, C_6H_3); IR (KBr) (cm^{-1}): 3069 (Ar–H), 1740 (C=O), 1260 (P=O), 744 (P–C); EIMS (probe) 70 eV, *m/z* (rel. int.): 324 $[M]^+$ (82.39), 138 (100), 109 (93.98), 93 (84.57); anal. calc. for $C_{12}H_{15}O_6PF_2$: C, 44.46, H, 4.66. Found: C, 44.65, H, 4.46%.

*3.3.12. O,O-Dimethyl 1-(3,5-difluorophenoxyacetoxy)trichloromethylmethylphosphonate (**5l**)*

Oil: yield 59.7%; n_D^{20} 1.4892; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 3.78–3.95 (m, 6H, $2OCH_3$), 4.86 (s, 2H, OCH_2CO), 5.96–5.99 (d, 1H, OCHP, J_{HP} = 13.3 Hz), 6.45–7.28 (m, 3H, C_6H_3); IR (KBr) (cm^{-1}): 3070 (Ar–H), 1747 (C=O), 1265 (P=O), 740 (P–C); EIMS (probe) 70 eV, *m/z* (rel. int.): 426 $[M]^+$ (28.72), 143 (94.93), 109 (1 0 0), 93 (94.17); anal. calc. for $C_{12}H_{12}Cl_3O_6PF_2$: C, 33.71, H, 2.83. Found: C, 33.68, H, 2.84%.

Acknowledgements

We gratefully acknowledge financial support of this work by National Basic Research Program of China (2003CB114400) and National Natural Science Foundation of China (Project No.: 20372023).

References

[1] J.T. Welch, Tetrahedron 43 (1987) 3123–3125.
[2] M. Hudlicky, Chemistry of Organic Fluorine Compounds II, American Chemical Society, Washington, DC, 1995, pp. 1119–1125.
[3] V.P. Kukhar, J. Fluorine Chem. 69 (1994) 199–205.
[4] Y.X. Liu, Q.Q. Zhao, Q.M. Wang, H. Li, R.Q. Huang, Y.H. Li, J. Fluorine Chem. 126 (2005) 345–348.
[5] X.Y. Xua, X.H. Qian, Z. Lia, G.H. Song, W.D. Chen, J. Fluorine Chem. 126 (2005) 297–300.

[6] X.M. Zheng, Z. Li, Y.L. Wang, W.D. Chen, Q.C. Huang, C.X. Liu, G.H. Song, J. Fluorine Chem. 123 (2003) 163–169.
[7] H.W. He, Z.J. Liu, Chin. J. Org. Chem. 21 (2001) 878–883.
[8] J.L. Brayer, L. Talinani, J. Tessier, EP 376819, 1990.
[9] H. Mccommbie, B.C. Sauaders, J. Chem. Soc. (1945) 380–382.
[10] ***6a**: O,O-dimethyl 1-(2,3-dichlorophenoxyacetoxy)ethylphosphonate*, oil, n_D^{20} 1.5131; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 1.48–1.54 (d, 3H, CH_3), 3.76–3.84 (m, 6H, $2OCH_3$), 4.80(s, 2H, OCH_2CO), 5.38–5.47 (m, 1H, OCHP, J_{HP} = 13.3 Hz), 6.79–7.17 (m, 3H, C_6H_3); IR (KBr) (cm^{-1}): 3077 (Ar–H), 1748 (C=O), 1264 (P=O), 740 (P–C); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 356 $[M]^+$ (41.55), 138 (91.87), 109 (100), 93 (69.22); anal. calc. for $C_{12}H_{15}Cl_2O_2P$: C, 40.36, H, 4.23. Found: C, 40.38, H, 4.10%. ***6b**: O,O-dimethyl 1-(2,3-dichlorophenoxyacetoxy)trichloromethylmethylphosphonate*, oil, n_D^{20} 1.5392; ^{1}H NMR (400 Hz, $CDCl_3$) δ: 3.86–3.93 (m, 6H, $2OCH_3$), 4.95 (s, 2H, OCH_2CO), 5.96–5.97 (d, 1H, OCHP, J_{HP} = 13.3 Hz), 6.79–7.16 (m, 3H, C_6H_3); IR (KBr) (cm^{-1}): 3078 (Ar–H), 1744 (C=O), 1263 (P=O), 744 (P–C); EIMS (probe) 70 eV, *m*/*z* (rel. int.): 458 $[M]^+$ (21.20), 109 (100), 93 (81.18); anal. calc. for $C_{12}H_{12}Cl_5O_6P$: C, 31.30, H, 2.63. Found: C, 31.41, H, 2.68%.
[11] A.H. Lu, W.H. He, J. Central. Cina. Normal. University (Nat. Sci.) 33 (4) (1999) 543–546.
[12] L.P. Meng, H.W. He, Z.J. Liu, HuBeiHuaGong (special issue) (1998) 40–41.
[13] H.W. He, T. Chen, T. Wang, CN 1560058A, 2005.
[14] F. Texier-Boullet, M. Leouitte, Tetrahedron Lett. 27 (30) (1986) 3515–3516.
[15] F. Texier-Boullet, A. Foucaud, Synthesis 11 (1982) 916–918.