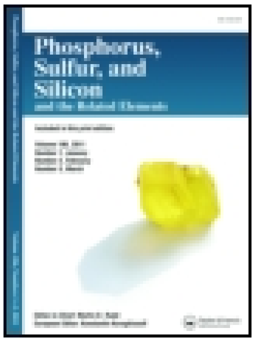

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Herbicidal activity and application cyclic of phosphonates

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ABSTRACT

Among alkylphosphonates **Io,** *O,O*-dimethyl 1-(2,4-dichlorophenoxyacetoxy) ethylphosphonate (clacyfos) was found to be an effective inhibitor against dicotyledons PHDc and exhibited excellent herbicidal activity in our previous work. According to our study on the alkylphosphonates **Io**, both R^1 and R^2 groups in the structural unit of phosphorus-containing played a very important role in herbicidal activity. Therefore, a series of 2-[1-(substituted phenoxycarboxy)alkyl]-5,5-dimethyl-1,3,2-dioxaphosphinane-2-one containing fluorine **II** was obtained by the modification of alkylphosphonates **Io**. The bioassay results showed that cyclic phosphonate **II-6** with CH_3 as R, 2-Cl,4-F as Y_n exhibited promising herbicidal activity. Its herbicidal activity, weed-controlling spectrum, selectivity between crops and weeds were further evaluated in greenhouse and field.

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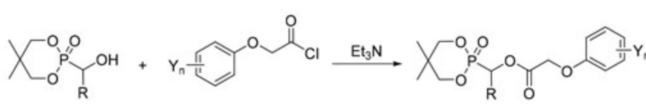
Cyclic alkylphosphonate; herbicidal activity; fluorine

GRAPHICAL ABSTRACT



1. Introduction

Organic phosphorus compounds display a wide range of biological activities and have attracted considerable attention in the field of pesticides.[1] A detailed study of acylphosphinates and acylphosphonates revealed that these analogs of pyruvate could be designed as mechanism-based inhibitors of pyruvate dehydrogenase complex (PDHc).[2] However, they are not active enough for full development as herbicides.[2,3] On the basis of acetylphosphonate as a hit compound, several series of 1-substituted alkylphosphonates **Io**, were designed and synthesized. Among alkylphosphonates **Io**, *O,O*-dimethyl 1-(2,4-dichlorophenoxyacetoxy)ethylphosphonate (clacyfos) was found to be an effective inhibitor against dicotyledons PHDc and exhibited excellent herbicidal activity in our previous work.[4] Clacyfos can be as herbicide against broad-leaved weeds, grass weeds, and sedges by post-emergence application.[5] These results encouraged us to make further modifications on the basis of the structure **Io**. According to our study on alkylphosphonates **Io**, both R^1 and R^2 groups in the structural unit of phosphorus-containing played a very important role in herbicidal activity. It was noticed that a variety of studies had demonstrated that bioactivity and stability of phosphonates or phosphates could be increased by introducing a phosphorus-containing heterocyclic moiety to their parent structure.[6,7] Considering the possible contribution of cyclophosphonate to herbicidal activity an open-chain *O,O*-dialkyl phosphonate unit in the structure of **Io** was further modified by introducing a six-membered cyclic phosphonate unit. Series of 2-[1-(substituted phenoxyacetoxy)alkyl]-5,5-dimethyl-1,3,2-dioxaphosphinane-2-one **II** were designed and synthesized (Scheme 1). Their herbicidal activity was tested, and active compound was further evaluated in greenhouse and field.

2. Results and discussion

2.1. Syntheses

Cyclic phosphonate **II** could be conveniently synthesized by the condensation of 2-(1-hydroxyalkyl)-5,5-dimethyl-1,3,2-dioxaphosphinane-2-one **M2** with an appropriate substituted phenoxyacetyl chloride **M4** in the presence of a base (Scheme 2). The addition of 1,3,2-dioxaphosphinane **M1** to various aldehydes gave corresponding cyclic 1-hydroxyalkylphosphonates **M2**. Considering the unique properties of fluorine, the 2-Cl,4-F, 2-F,4-Cl, 2-F, 4-F or 3-CF_3 group as Y_n was introduced into substituted phenoxyacetic acid respectively. A series of cyclic phosphonates **II** containing fluorine including **II 1-18** has been synthesized by this way (Table 1).[8]

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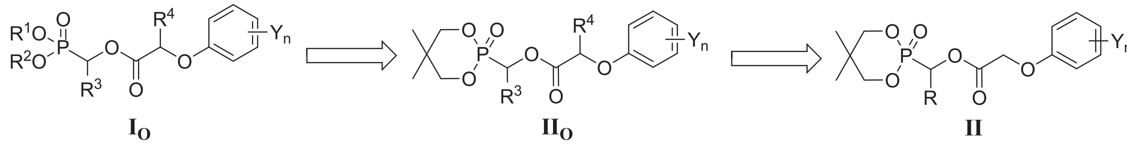
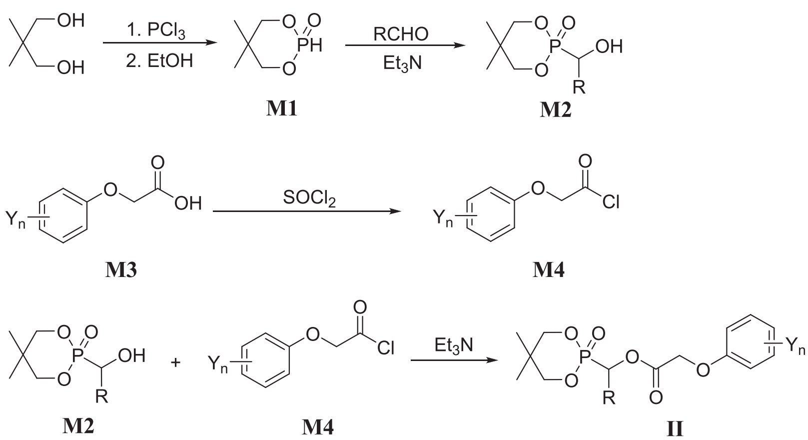


Scheme 1. Design of cyclic phosphonates.



Scheme 2. Synthesis of cyclic phosphonates **II**.

2.2. Herbicidal activity

All of these cyclic phosphonates **II** containing fluorine exhibited moderate to good herbicidal activities by a preliminary test.[6] The results showed fluorine or trifluoromethyl group as Y_n on benzene ring had a very important effect on herbicidal activity. A satisfactory herbicidal activity required a reasonable combination both type and position of Y_n. Compound **II-6** with CH_3 as R, 2-Cl,4-F as Y_n was found to have best herbicidal activity among those compounds **II 1-18**. The post-emergence herbicidal activity and weed-controlling spectrum of **II-6** were further examined.

As shown in Table 2, **II-6** displayed significant inhibition against common amaranth, goosefoot, leaf mustard, and morning glory at 37.5 and 18.75 g ai/ha, respectively. It exhibited better herbicidal activity against tested broad-leaved weeds than that of 2,4-D and glyphosate even at 18.5 g ai/ha. **II-6** showed broad-spectrum activity to control broad-leaved weeds included common amaranth (*Amaranthus retroflexus*), goosefoot (*Chenopodium album*), leaf mustard (*Brassica juncea*), morning glory (*Ipomoea nil*), monarch redstem (*Ammannia baccifera*), pickerel weed (*Monochoria vaginalis*), ball cabbage (*Brassica oleracea*), wild vetch (*Vicia gigantea*), chili (*Capsicum annuum*), curled dock (*Rumex crispus*), chingma abutilon (*Abutilon theophrasti*), alligatorweed (*Alternanthera philoxeroides*), field chickweed (*Cerastium arvense*), white eclipta (*Eclipta prostrata*) at 150 g ai/ha. Crop selectivity and safety evaluation of **II-6** were carried out by post-emergence spray treatment. The results showed **II-6** could result in injury to dicotyledonous crops, such as green vegetable, tomato, radish, chili, cotton, rape, and soybean even at 75 g ai/ha. However wheat, maize, and rice exhibited higher tolerance to **II-6** even at 150–600 g ai/ha.

In order to evaluate the efficacy of **II-6** against weeds in field condition, the field trial was conducted in maize field at Shandong in China. A formulation of 10% EC was used in the field testing. 10% **II-6** EC was tested in the maize field against primary broad-leaved weeds at 300-600 g ai/ha in Shandong when weeds were at 3 to 5 leaves stage and maize was at 4 to 6 leaves stage. 57% 2,4-D butyl ester EC was used at a recommended rate 513 g ai/ha as a positive control. The results showed that 10% **II-6** EC exhibited 90-100% inhibitory activity against white eclipta (*Eclipta prostrate*), Asian copperleaf (*Acalypha australis*), chingma abutilon (*Abutilon theophrasti*), goosefoot (*Chenopodium album*), bunge's smartweed (*Polygonum bungeanum*), Sibirian cocklebur (*Xanthium strumarium*) and black nightshade (*Solanum nigrum*) at 300–360 g ai/ha in maize field (Table 3). No evident injury of maize was observed in all treatments even at 600 g ai/ha by **II-6** during experimental period.

Table 1. Structure of cyclic phosphonates containing fluorine **II**.

Compd.	R	Y_n	Compd.	R	Y_n
II-1	CH_3	H	**II-10**	Ph	3-CF_3
II-2	CH_3	2-F	**II-11**	Ph	2-F, 4-Cl
II-3	CH_3	4-F	**II-12**	Ph	2-Cl, 4-F
II-4	CH_3	3-CF_3	**II-13**	2-Furyl	H
II-5	CH_3	2-F,4-Cl	**II-14**	2-Furyl	2-F
II-6	CH_3	2-Cl,4-F	**II-15**	2-Furyl	4-F
II-7	Ph	H	**II-16**	2-Furyl	3-CF_3
II-8	Ph	2-F	**II-17**	2-Furyl	2-F, 4-Cl
II-9	Ph	4-F	**II-18**	2-Furyl	2-Cl, 4-F

3. Conclusions

Cyclic phosphonates containing fluorine **II 1-18** were designed and prepared based on the modification of open-chain 1-substituted alkylphosphonates **Io**. Their herbicidal activity was further evaluated in greenhouse and field. Cyclic phosphonate **II-6** (R = Me, Y_n = 2-Cl,4-F) was found to be most active compound with good selectivity between dicotyledonous weeds and monocotyledonous crops. **II-6** exhibited

Table 2. The post-emergence herbicidal activity of **II-6**.

Compd.	Rate (g ai/ha)	Amr[b]	Che[b]	Brj[b]	Ipn[b]
II-6	37.5	95	75	100	90
	18.75	90	70	95	90
2,4-D	37.5	90	80	100	100
	18.75	70	75	80	90
Glyphosate	37.5	60	70	75	60
	18.75	60	50	70	50
Clacyfos	37.5	100	80	100	100
	18.75	90	70	100	100

[a]Inhibitory potency (%) against the growth of plants in the greenhouse, 0 (no effect), 100% (completely kill).
[b]Amr: common amaranth; Che: goosefoot; Brj: leaf mustard; Ipn: morning glory.

Table 3. Post-emergence herbicidal activity of 10% **II-6** EC in maize field.

	Inhibitory potency % (45 DAT)						
Rate g ai/ha	Ecl[c]	Aca[c]	Abu[c]	Che[c]	Pol[c]	Xan[c]	Sol[c]
300	92	100	95	96	95	90	90
360	96	100	97	100	100	95	95
450	98	100	100	100	100	100	98
600	100	100	100	100	100	100	98
57% 2,4-D butyl ester EC 513	95	100	96	96	98	98	97

[a]Inhibitory potency (%) was measured as percentage change in each weed fresh weight compared to that of the untreated control; values are the average of 4 replicates. DAT is day after treatment.
[b]Application method: Spray one time by a Jacto PJ-16 or Matabi sprayer.
[c]Ecl: white eclipta, Aca: Asian copperleaf, Abu: chingma abutilon, Che: goosefoot, Pob: bunge's smartweed, Xan: Siberian cocklebur, Sol: black nightshade.

broad weed-controlling spectrum and good inhibitory activity against broad-leaved weeds at 150c–18.5 g ai/ha, which were comparable to 2,4-D and glyphosate. It is safe for wheat, maize and rice especially.

Field data showed that **II-6** exhibited good post-emergence herbicidal effect against main weeds in maize field and very safe for maize at 300–450 g ai/ha. Therefore it displayed potential utility as a selective post-emergence herbicide for weed control in monocotyledonous crops fields. It would be promising that **II-6** as post-emergence herbicide for weed control in wheat or rice field.

3.1. Experimental greenhouse herbicidal activity

Weed seeds were planted in 9 cm-diameter plastic boxes containing artificial mixed soil. Before plant emergence, the boxes were covered with plastic film to keep moist. Plants were grown in the greenhouse. Fresh weight of the above ground tissues was measured 10 days after treatment. The inhibition percent is used to describe the control efficiency of compounds. All test compounds were dissolved in N,N-dimethylformamide with the addition of a little Tween 20 and then were sprayed using a laboratory belt sprayer delivering at 750 L/ha spray-volume. The mixture of the same amount of water, N,N-dimethylformamide and Tween 20 was sprayed as control.

3.2. Crop selectivity

Conventional rice, corn, cotton, soybean, rape, and wheat were respectively planted in plots (diameter =12 cm) containing test soil and grown in a greenhouse at 20–25 °C. After the plants had reached the four-leaf stage, the spraying treatment was conducted at different dosages by diluting the formulation of the selected compounds. The visual injury and growth state of the individual plant were observed at regular intervals. The final evaluation for crops safety of the selected compounds was conducted by visual observation in 30 days after treatment on the 0–100 scale (0 = no injury, 10 = chlorosis, 100 = death).

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