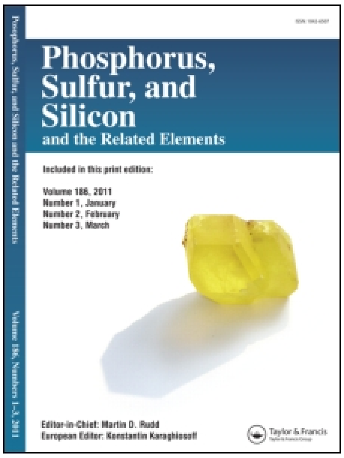

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ORGANIC PHOSPHORUS COMPOUNDS 93.[1] PREPARATION, PROPERTIES AND HERBICIDAL ACTIVITY OF 2-SUBSTITUTED 5-PHENOXY- AND 5-PYRIDY LOXY-PHENYLAMINOALKYLPHOSPHONIC-AND-PHOSPHINIC ACILAS WELL AS-PHOSPHINE OXIDE DERIVATIVES*

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ORGANIC PHOSPHORUS COMPOUNDS 93.[1] PREPARATION, PROPERTIES AND HERBICIDAL ACTIVITY OF 2-SUBSTITUTED 5-PHENOXY- AND 5-PYRIDYLOXY-PHENYLAMINOALKYL-PHOSPHONIC- AND -PHOSPHINIC ACID—AS WELL AS—PHOSPHINE OXIDE DERIVATIVES*

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Dedicated in friendship to Professor Dr. L. Horner on the occasion of his 80th birthday

(Received August 3, 1990)

Interaction of 4-phenoxy and 4-pyridyloxy substituted 1,2-dinitrobenzenes and aminoalkylphosphonates, -phosphinates, and -phosphine oxides produces mainly 5-phenoxy- and 5-pyridyloxy substituted 2-nitrophenylaminoalkylphosphonates, -phosphinates and -phosphine oxides (Table I to IV and Figure 1 to 5), some of which show high herbicidal and plant growth regulating activity. The herbicidal activity increases from pyridyloxy-phenylaminoalkylphosphonates to phenoxy-phenylaminoalkyl-phosphonates, -phosphinates, -phosphine oxides. Of all the compounds tested the phosphine oxide **4a** was at all concentrations the most active compound.

Key words: 5-Phenoxy- and 5-pyridyloxy-2-nitrophenylaminoalkylphosphonates, -phosphinates, and -phosphine oxides; NMR-spectra; PGR and herbicidal activity.

INTRODUCTION

A few years ago we described the preparation and reactions of phenoxyphenylphosphonates and -phosphinates and showed that some of these compounds exhibited a higher herbicidal activity than the commercial products bifenox and acifluorfen, but their selectivity was not as good.[2] Now we have studied the reaction of substituted 1,2-dinitrodiphenylethers with aminoalkylphosphonates, -phosphinates and -phosphine oxides and have determined the herbicidal activity of these compounds.[3,4]

RESULTS AND DISCUSSION

1,2-Dinitro-4-(2'-chloro-4'-trifluoromethylphenoxy)-benzene reacts readily with aminoalkylphosphonates, -phosphinates, and -phosphine oxides with substitution of one nitro group and yields the corresponding phosphonates, phosphinates and phosphine oxides in good yields, e.g.

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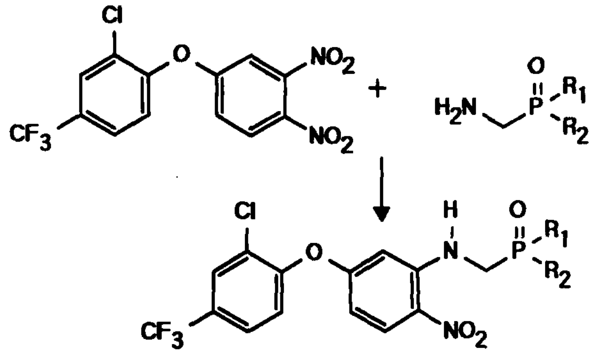
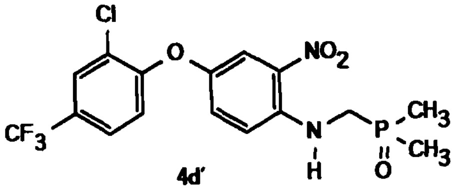
*Extended version of a poster (7th International Congress of Pesticide Chemistry, Hamburg, FRG, August 5-10th, 1990)



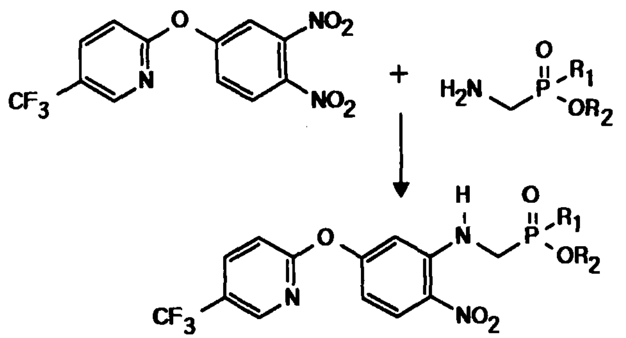
1. $R_1,R_2 = OR$ 3. R_1 = alkyl, $R_2 = OR$ 4. R_1,R_2 = alkyl

When carrying out the above reaction with aminomethyldimethylphosphine oxide in refluxing toluene a 1.2% yield of 2-nitro-4-(2'-chloro-4'-trifluoromethylphenoxy)-phenyl-aminomethyl-dimethylphosphine oxide (**4d'**) was isolated in addition to 70% **4d** (R_1, R_2 = CH_3). Thus the reaction is not completely regiospecific.



4d'

The same reaction can also be applied for the preparation of pyridyloxy-phenylaminoalkylphosphonates and -phosphinates.



2, R_1 = alkyl or OR

Hydrolysis of the esters **1** to **3** with 6N HCl under reflux yields the corresponding acids in nearly quantitative yield.

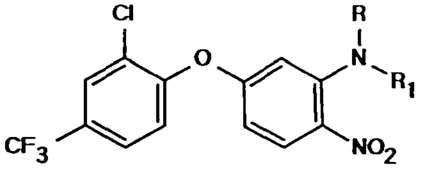
After completion of our work we learned that two other groups[5,6] have also studied the reaction of 1,2-dinitrodiphenylethers with aminoalkylphosphonates.

Herbicidal Activity

Several of the substituted phenoxy- and pyridyloxy-phenylaminoalkylphosphonates, -phosphinates, and -phosphine oxides (Table I–IV) exhibit high herbicidal

TABLE I

Physical properties of 2-nitro-5-(2′-chloro-4′-trifluoromethylphenoxy)-phenylaminoalkylphosphonates



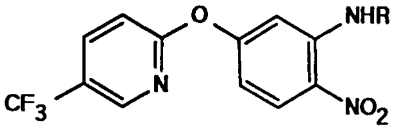
				^{1}H-NMR							
R	R$_1$	Yield (%)	m.p. °C	Solvent	CH$_2$P	(J_{PCH})	NCH$_2$	OCH	OH	OCH$_2$	arom. H see ex 3
H	$(EtO)_2P(O)CH_2CH_2$	89.2	yellow oil[a]	$CDCl_3$	2.23	(*J* 18)	3.6			4.23	
H	$(EtO)_2P(O)CH_2$	58	78–79.5[b]	$CDCl_3$	3.73	(*J* 13)				4.27	
H	$[(EtO)_2P(O)]_2CH$	41.2	yellow oil	$CDCl_3$	3.7	(*m*)				4.17	
H	$(i\text{-}PrO)_2P(O)CH_2\text{-}CH_2$	82.3	orange oil	$CDCl_3$	2.1	(*J* 18)	3.5	4.7			
H	$(i\text{-}PrO)_2P(O)CH\text{-}(CH_3)$	95	orange oil	$CDCL_3$	3.8	(*m*)		4.77			
H	$(i\text{-}PrO)_2P(O)CH_2$	57.6	93–94	$CDCl_3$	3.43	(*J* 14)		4.7			
H	$(i\text{-}PrO)_2P(O)CH_2\text{-}CH_2CH_2$	85.3	orange oil	$CDCl_3$	2	(*m*)	3.4	4.75			
CH_3	$(HO)_2P(O)CH_2$	64.5	126–128	CD_3OD	3.3	(*J* 14)					
CH_3	$(i\text{-}PrO)_2P(O)CH_2$	78.7	orange oil	$CDCl_3$	3.57	(*J* 9)	3.03	4.7			
$C_6H_5CH_2$	$(i\text{-}PrO)_2P(O)CH_2$	16.9	yellow oil	$CDCl_3$	3.47	(*J* 8)	4.57	4.7			
H	$(HO)_2P(O)CH_2CH_2$	68.7	226–227.5	CD_3OD	2.33	(*J* 18)	3.4		5.17		
H	$(HO)_2P(O)CH_2\text{-}CH_2CH_2$	91.3	152–154.5	CD_3OD	1.55	(*m*)	3.03		4.8		
H	$(HO)_2P(O)CH_2$	92	148–150	CD_3OD	3.37	(*J* 13)			4.93		
H	$[(HO)_2P(O)]_2CH$	82	190 (dec.)	CD_3OD	3.8	(*J* 21)			5.15		
H	$(EtO)_2P(O)CH\text{-}(CH_2C_6H_4Br\text{-}4)$	60.6	yellow resin	$CDCl_3$	2.8–3.5					4.2	

orange oil;

m.p. 74–76°C.

TABLE II

Physical properties of 2-nitro-5-(5-trifluoromethyl-2-pyridyloxy)-phenyl aminoalkylphosphonates and -phosphinates, **2**

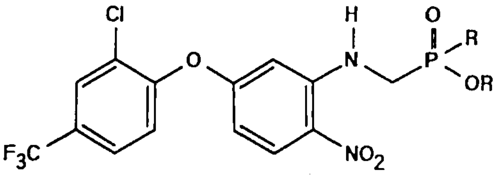


2

No.	R	Yield %	m.p. °C	^{1}H-NMR						^{31}P-NMR
				Solvent	CH_2P	NCH_2	OCH_2	OCH	OH	
a	$(EtO)_2P(O)CH_2$	48.7	74–76	$CDCl_3$	3.7(*J* 14)		4.2			20.93
b	$(EtO)_2P(O)CH_2CH_2$	98.5	orange oil	$CDCl_3$	2.25(*J* 18)					27.82
c	$(i\text{-}PrO)_2P(O)CH_2\text{-}CH_2CH_2$	43.9	81–82	$CDCl_3$	2.0(*m*)	3.4		4.73		28.47
d	$(HO)_2P(O)CH_2\text{-}CH_2CH_2$	80.6	134–136	CD_3OD	1.6(*m*)	3.0			4.8	
e	$(HO)_2P(O)CH_2$	96.9	94 (dec.)	CD_3OD						19.07
f	$(i\text{-}PrO)_2P(O)CH_2\text{-}CH_2$	48.8	81–83	$CDCl_3$	2.17(*J* 18)	3.32		4.8		25.49
g	$(HO)_2P(O)CH_2CH_2$	94.3	105–106	CD_3OD	1.8(*J* 18)	3.17			5.15	
h	$(EtO)CH_3P(O)CH_2$	28	88–90	$CDCl_3$	3.6(*J* 11)	1.6(*J* 14) PCH_3	4.17			

TABLE III

Physical properties of 2-nitro-5-(2′-chloro-4′-trifluoromethylphenoxy)-phenylaminomethylphosphinates, **3**



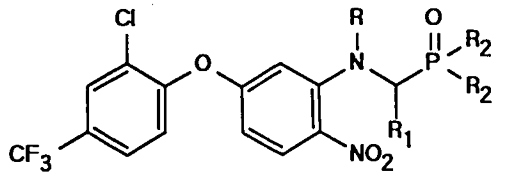
3

No.	R	R_1	Yield %	m.p.	^{1}H-NMR					^{31}P-NMR
					Solvent	R—P	CH_2P	OCH_2	OH	
a	CH_3	C_2H_5	76.6	118.5–119.5	$CDCl_3$	1.6(13)	3.6(*J* 11)	4.13		46.89
b	C_2H_5	C_2H_5	51.9	yellow oil	$CDCl_3$	0.9–2.1(*m*)	3.77(*J* 10)	4.2		
c	CH_3	H	96.8	153–154.5	CD_3OD	1.4(*J* 14)	3.5(*J* 10)		4.8	41.03 (DMSO)
d	C_2H_5	H	96.7	122–124	DMSO	0.7–2.0(*m*)	3.57(*J* 9)		7.2	44.19

and plant growth regulating properties. It would seem that only those compounds are herbicidally active which have a 5-phenoxy- or pyridyloxy substituent, whereas the one compound with a 4-phenoxysubstituent (**4d′**) is inactive. In the Figures 1–4 are shown the average herbicidal activities of the compounds tested against 4 weeds in the preemergent test and 7 weeds (3 monocotyledonous and 4 dicotyledonous) in the postemergent test at 4 kg/ha. Inspection of the curves shows that the herbicidal activity increases from pyridyloxy-phenylaminoalkylphosphonates (Figure 2) to phenoxy-phenylaminoalkyl-phosphonates (Figure 1) to phenoxy-

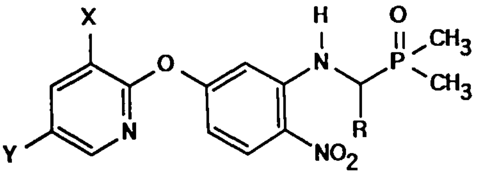
TABLE IV

Physical Properties of 2-nitro-5-(2′-chloro-4′-trifluoromethylphenoxy)-phenylaminoalkylphosphine oxides, **4a–h**, and 2-nitro-5-(subst.-2-pyridyloxy)-phenylaminoalkyl-phosphine oxides, **4e–g**



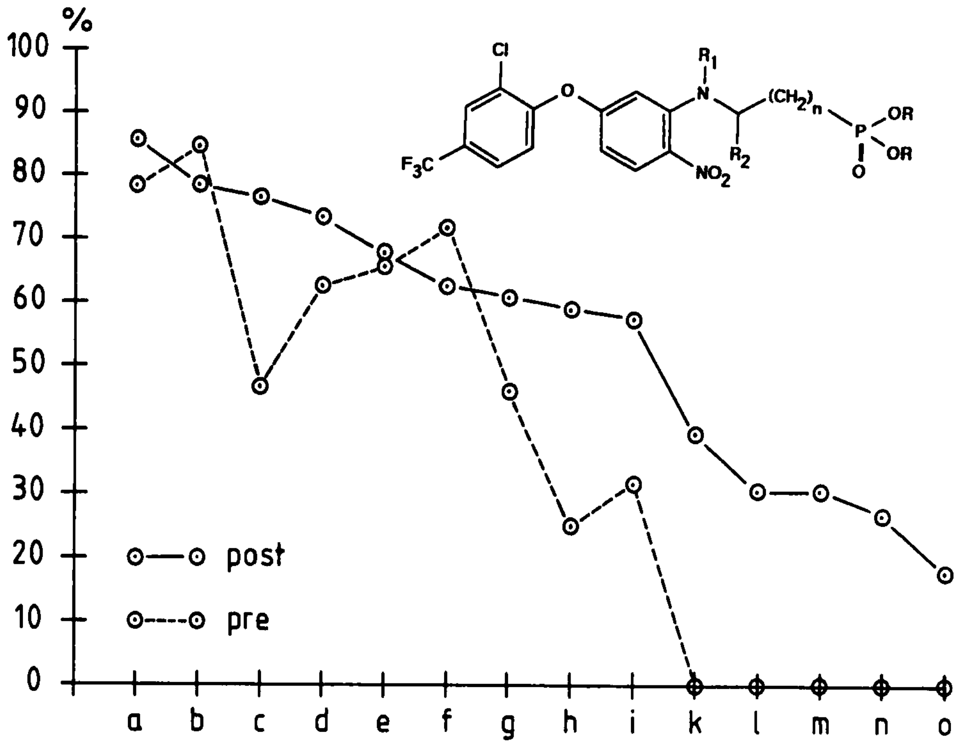
4

No.	R	R_1	R_2	Yield %	m.p. °C	Solvent	¹H-NMR P-CH_3	¹H-NMR P-CH_2	³¹P-NMR
a	H	CH_3	CH_3	41.2	151–153	$CDCl_3$	1.53(*J* 12)	3.8(*m*)	46.24
b	*n*-C_3H_7	H	CH_3	17.6	resin	$CDCl_3$	1.5(*J* 13)	3.55(*J* 7)	
c	H	H	C_2H_5	71	103–105	$CDCl_3$	0.9–2.1(*m*)	3.6(*J* 7)	48.47
d	H	H	CH_3	70	166–168	$CDCl_3$	1.63(*J* 13)	3.7(*J* 7)	40.1
h	H	3-CH_3C_6-H_4CH_2	CH_3	43.3	161–165	$CDCl_3$	1.5(2d, *J* 12)	2.8–4.0(*m*) (CH_2CHP)	



No.	R	X	Y	Yield %	m.p. °C	Solvent	P-CH_3	P-CH_2	³¹P-NMR
e	CH3	H	CF_3	41.2	180–181	$CDCl_3$	1.2(*J* 12)	3.9(*m*)	
f	H	Cl	Cl	49.6	153–154	$CDCl_3$	1.6(*J* 12.6)	3.65(*J* 8)	41.96
g	H	H	CF_3	70.2	158–160	$CDCl_3$	1.65(*J* 12.8)	3.7(*J* 7)	40.56

phenylaminoalkylphosphinates (Figure 3) to phenoxy-phenylaminoalkylphosphine oxides (Figure 4). Whereas pyridyloxy-phenylaminoalkylphosphonates (**2**) show no preemergent herbicidal activity, the preemergent activity of the compounds **1**, **3** and **4** goes in general parallel with the postemergent activity with the exception of the phosphonic acid derivatives **1k** to **1o**, which are inactive. This is probably due to the adsorption of the phosphonic acids in the soil. Much less difference exists in the phosphinate series (Figure 3). The phosphinic acids **3c** and **3d** have nearly the same activity pre- and postemergent as the esters **3a** and **3b**. And finally in the phosphine oxide series the preemergent activity of several derivatives (**4c–4f**, and **4h**) is higher than the postemergent activity. The dependence of the preemergent herbicidal activity of the most active compound in each series (**1b**, **3a**, **4a**; because of low activity the pyridyloxy-derivatives **2** have not been included) from the concentration against 4 monocotyledonous and 7 dicotyledonous weeds is shown in Figure 5. At all concentrations the phenoxy-phenylaminoethyl-dimethylphosphine oxide **4a** is the most active compound followed by **1b** and then **3a**. All three compounds show a high selectivity in rice.



	a	b	c	d	e	f	g	h	i	k	l	m	n	o
n	1	0	0	1	0	0	2	0	0	0	1	2	0	0
R	Et	Et	Et	iPr	iPr	iPr	iPr	H	iPr	iPr	H	H	H	H
R_1	H	H	H	H	H	H	H	Me	Me	Bz	H	H	H	H
R_2	H	H	PO_3Et_2	H	Me	H	H	H	H	H	H	H	H	PO_3H_2

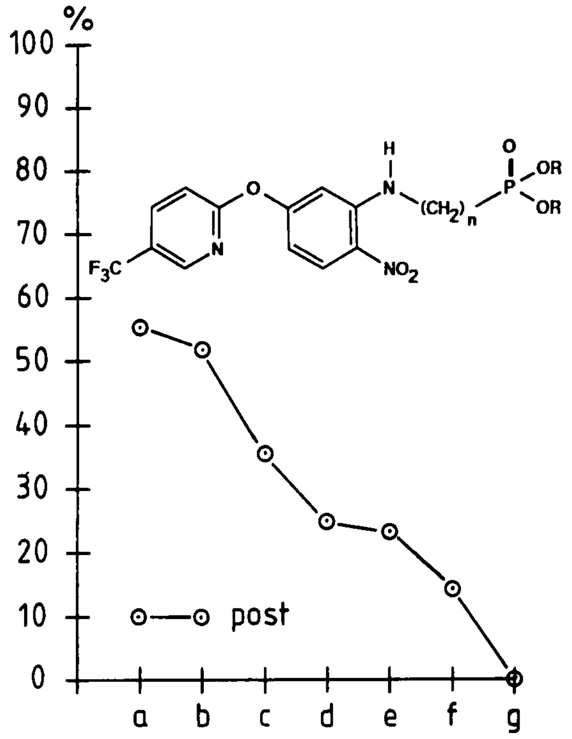
FIGURE 1 Herbicidal Activity of Phenoxy-phenylaminoalkylphosphonates at 4 kg/ha in the Greenhouse

EXPERIMENTAL

Phosphorus NMR-spectra were recorded using a Bruker WP 80 spectrometer at 32.28 MHz (Reference 85% H_3PO_4), and ^{1}H-NMR-spectra were recorded with a Varian EM 360 spectrometer at 60 MHz or a Bruker WM 250/250 MHz spectrometer [Reference $(CH_3)_4Si$]. The chemical shifts are reported in ppm with negative values being upfield of the standard, and positive downfield. The reactions with trivalent phosphorus compounds were run under argon.

The aminoalkylphosphonates, -phosphinates and -phosphine oxides, used as starting materials, have been prepared according to literature procedures.[7,8,9] Dinitrodiphenylethers were available from a previous study.[2]

1. 2-Nitro-5-(2'-chloro-4'-trifluoromethylphenoxy)-phenylaminomethylphosphonic acid di-isopropyl ester, **1f**. A mixture of 23.2 g (0.064 mol) of 3,4-dinitro-2' chloro-4'-trifluoromethyl-diphenylether[10] and 25 g (0.128 mol) of 0,0-diisopropyl-aminomethylphosphonate, dissolved in 120 ml of toluene, is heated to reflux for 16 hours. Then the dark solution is treated with carbon black, filtered and the filtrate evaporated on a rotavapor to give 31.38 g (= 96%) of an orange oil which crystallizes on standing at room temperature, m.p. 82–84°C. Recrystallization from di-isopropyl ether gives 18.84 g (57.6%) pure **1f**, m.p. 94–94°C, yellow needle-like crystals.



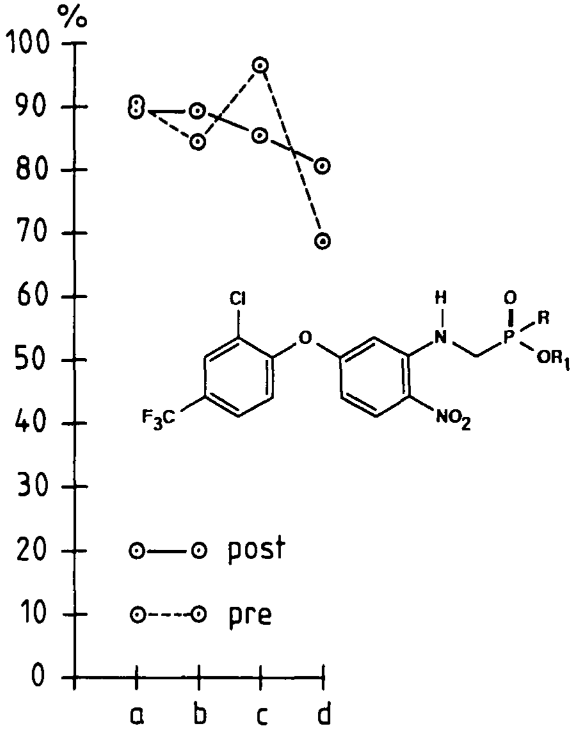
	a	b	c	d	e	f	g
n	1	2	3	3	1	2	2
R	Et	Et	iPr	H	H	iPr	H

FIGURE 2 Herbicidal Activity of Pyridyloxyphenylaminoalkylphosphonates at 4 kg/ha in the Greenhouse

$C_{20}H_{23}ClF_3N_2O_6P$ (510.8) calc: C 47.03, H 4.54, N 5.48, F 11.16, Cl 6.94%; found C 47.07, H 4.82, N 5.46, F 10.43, Cl 6.56%;
^{1}H-NMR ($CDCl_3$) δ = 1.23 (2d, $CH_3)_2$, 12H); 3.43 (2*d*, J_{PCH} 14, P_{NCH} 5, CH_2P, 2H; 4.7(*m*, OCH, 2H); 6.17–8.3(*m*, C_6H_3, 6H); 8–8.5(br, NH, 1H) [ppm].
^{31}P-NMR ($CDCl_3$) 18.7 ppm

2. 2-Nitro-5-(2' chloro-4'-trifluoromethylphenoxy)-phenylaminomethylphosphonic acid, **In**. A mixture of 3 g (5.9 mmol) of **If** and 100 ml of **6N** HCl is refluxed for 16 hours and then the solution evaporated on a rotavapor. As a residue is obtained 2.3 g (92%) of **In**, yellow crystals, m.p. 148–150°C.
$C_{14}H_{11}ClF_3N_2O_6P$ (426.6) calc: C 39.41, H 2.60, N 6.57%; found: C 39.1, H 2.80, N 6.7%
^{1}H-NMR (CD_3OD) δ = 3.37(*d*, J_{PCH} 13, CH_2P, 2H); 4.9(*s*, OH, NH); 5.8–8.0(*m*, C_6H_3, 6H) [ppm]

3. 2-Nitro-5-(2'-chloro-4'-trifluoromethylphenoxy)-phenylaminomethylphosphonic acid diethyl ester, **Ib**. To a refluxing solution of 20 g (0.055 mol) of 3,4-dinitro-2'-chloro-4'-trifluoromethyl-diphenyl ether in 100 ml of toluene is dropwise added 18.43 g (0.11 mol) of 0,0-diethyl-aminomethyl-phosphonate. Then the mixture is refluxed for 18 hours, evaporated on a rotavapor and the residue, an orange oil, chromatographed (silica gel F60, eluent ethylacetate). There is obtained 14.38 g (58%) **Ib**, m.p. 78–79°C, yellow needles from diisopropyl ether.
$C_{18}H_{19}ClF_3N_2O_6P$ (482.78) calc: C 44, 78, H 3.96, N 5.80, Cl 7.34, P 6.4%; found C 44.71, H 4.03, N 5.78, Cl 7.35, P 6.39%;



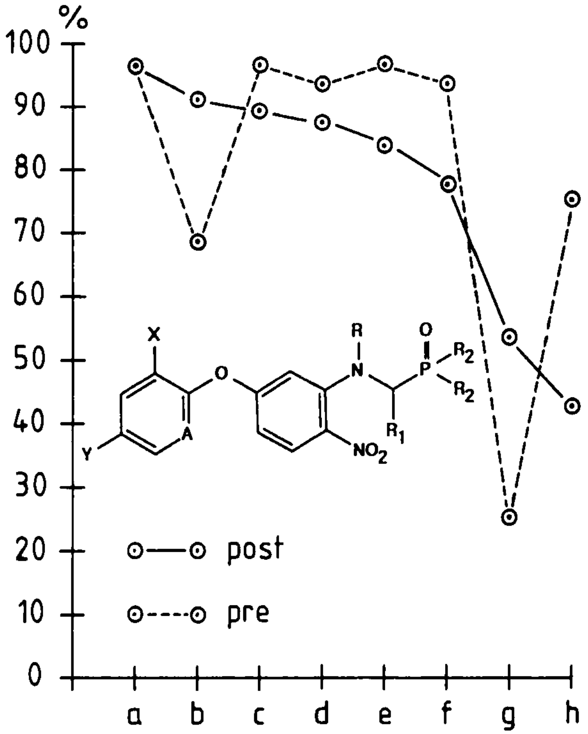
	a	b	c	d
R	Me	Et	Me	Et
R$_1$	Et	Et	H	H

FIGURE 3 Herbicidal Activity of Phenoxyphenylaminomethylphosphinates at 4 kg/ha in the Greenhouse

^{1}H-NMR ($CDCl_3$) δ = 1.4(*t*, CH_3, 6H); 3.73(2*d*, J_{PCH}, 13, J_{NHCH} 5, CH_2P, 2H); 4.27(qui, OCH_2, 4H); 6.3(2*d*, CH-4, 1H); 6.57(*d*, CH-6, 1H); 7.35(*d*, CH-6′, 1H); 7.7(2*d*, CH-5′, 1H); 7.83(*d*, CH-3′, 1H); 8.2(*d*, CH-3, 1H); 8.4(qu., J_{PCNH} 5, J_{NHCH} 5, NH, 1H) [ppm]
^{31}P-NMR ($CDCl_3$) 20.93 ppm
The compounds listed in Table I were prepared in a similar way.

4. 2-Nitro-5-(5′-trifluoromethyl-2′ pyridyloxy)-phenylaminomethylphosphonic acid diethyl ester **2a**. To 15 g (0.045 mol) of (5′-trifluoromethyl-2′-pyridyloxy-)-3,4-dinitrobenzene dissolved in 50 ml toluene is added dropwise under reflux 7.6 g (0.045 mol) of 0,0-diethyl-aminomethylphosphonate. Then the mixture is refluxed for 12 hours, evaporated on a rotavapor, and the residue chromatographed (silica gel, eluent hexan:ethylacetate 1:4). There is obtained 9.8 g (48.7%) **2a,** m.p. 74–76°C, slightly yellow crystals.
$C_{17}H_{19}F_3N_3O_6P$ (449.3) calc: C 45.44, H 4.26, N 9.35, P 6.89%; found C 44.2, H 4.2, N 10.1, P 6.8%
^{1}H-NMR ($CDCl_3$) δ = 1.37(*t*, CH_3, 6H); 3.7(2*d*, J_{PCH} 14, J_{NHCH} 6, CH_2P, 2H), 4.2(qui, OCH_2, 4H); 6.5(2d, CH-4, 1H); 6.78(*d*, CH-6, 1H); 7.15–8.5(*m*, aromat. CH + NH, 5H) [ppm]
The compounds listed in Table II were prepared in a similar way.

5. O-Ethyl-2-nitro-5-(2′-chloro-4′-trifluoromethylphenoxy)-phenylaminomethyl-methylphosphinate, **3a**. To a refluxing solution of 19.8 g (0.055 mol) of 3,4-dinitro-2′-chloro-4′-trifluoromethyl-diphenylether in 100 ml of toluene is slowly added 15 g (0.1084 mol) of O-ethyl-aminomethyl-methyl-phosphinate and then the solution refluxed for a further 30 hours. The solution is evaporated on a rotavapor and the



	a	b	c	d	e	f	g	h
R	H	Pr	H	H	H	H	H	H
R_1	Me	H	H	H	Me	H	H	3-MePhCH$_2$
R_2	Me	Me	Et	Me	Me	Me	Me	Me
X	Cl	Cl	Cl	Cl	H	Cl	H	Cl
Y	CF$_3$	CF$_3$	CF$_3$	CF$_3$	CF$_3$	Cl	CF$_3$	CF$_3$
A	CH	CH	CH	CH	N	N	N	CH

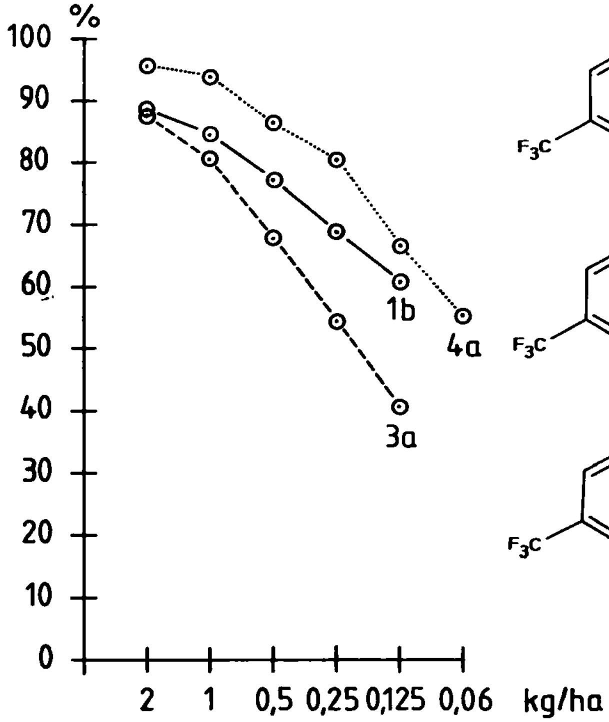
FIGURE 4 Herbicidal Activity of Phenoxy- and Pyridyloxyphenylaminoalkylphosphine oxides at 4 kg/ha in the Greenhouse

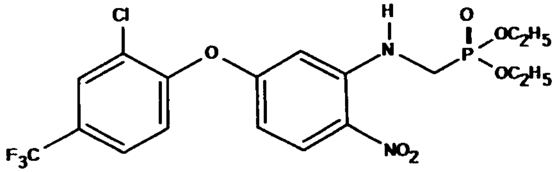
residue chromatographed (silica gel; eluent ethylacetate). There is obtained 19.07 g (76.6%) **3a**, m.p. 118.5–119.5°C.

$C_{17}H_{17}ClF_3N_2O_5P$ (452.7) calc: C 45.10, H 3.78, N 6.19, P 6.84%; found: C 44.94, H 3.89, N 6.34, P 6.79%;

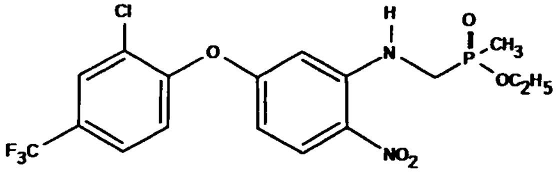
^{1}H-NMR ($CDCl_3$) δ = 1.4(*t*, CH_3, 3H); 1.6(*d*, J_{PCH} 13, PCH_3, 3H); 3.6(*dd*, J_{PCH} 11, CH_2P, 2H); 4.13(qui, OCH_2, 2H); 6.3(2*d*, CH-4, 1H); 6.5(*d*, CH-6, 1H); 7.25(*d*, CH-6', 1H); 7.6(2*d*, CH-5', 1H); 7.8(*d*, CH-3', 1H; 8.2(*d*, CH-3, 1H; 8.4(br, NH, 1H) [ppm]

6. *2-Nitro-5-(2'-chloro-4'-trifluoromethylphenoxy)-phenylaminomethyl-dimethylphosphine oxide*, **4d**. To a refluxing solution of 18.13 g (0.05 mol) of 3,4-dinitro-2'-chloro-4'-trifluoromethyl-diphenylether in 50 ml of toluene is dropwise added 10.71 g (0.1 mol) of molten aminomethyl-dimethylphosphine oxide. The solution is refluxed for a further 2 hours, then evaporated on a rotavapor. The residue is chromatographed on silica gel using ethylacetate/ethanol (4:1) as eluent. There are obtained two fractions. Fraction 1: 14.8 g (70%) **4d**, yellow crystals m.p. 166–168°C

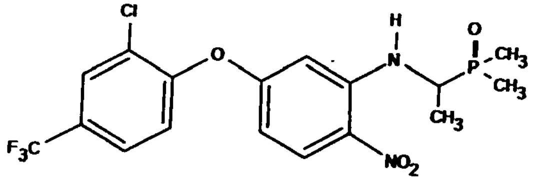




Ib



3a



4a

FIGURE 5 Dependence of the Premergent Herbicidal Activity of **1b**, **3a**, and **4a** from the Concentration against four Monocotyledonous and seven Dicotyledonous Weeds

$C_{16}H_{15}ClF_3N_2O_4P$ (422.7) calc: C 46.46, H 3.58, N 6.63, F 13.48, Cl 8.39, P 7.33%; found C 45.5, H 3.6, N 6.9, F 13.4, Cl 8.3, P 7.5%;

^{1}H-NMR ($CDCl_3$) δ = 1.63(*d*, J_{PCH} 13, CH_3P, 3H); 3.7(*dd*, J_{PCH} 7, CH_2P, 2H); 6.25(2*d*, CH-4, 1H); 6.6(*d*, CH-6, 1H); 7.25(*d*, CH-6′, 1H); 7.6(2d, CH-5′, 1H); 7.8(*d*, CH-3′, 1H); 8.2(*d*, CH-3, 1H); 8.5(qu, J5, NH, 1H) [ppm]

Fraction 2: 0.25 g (1.2%), 2-nitro-4-(2′-chloro-4′-trifluoromethylphenoxy)-phenylaminomethyl-dimethylphosphine oxide, **4d**, orange red crystals, m.p. 150–152°C (from ethylacetate/diisopropylether)

^{1}H-NMR ($CDCl_3$) δ = 1.6(*d*, J_{PCH} 12, CH_3P, 3H); 3.73(2*d*, J_{PCH} 6, CH_2P, 2H); 6.93(*d*, CH-6, 1H); 7.2(*d*, CH-6′, 1H); 7.35(2*d*, CH-5, 1H); 7.5(2*d*, CH-5′, 1H); 7.75(*d*, CH-3′, 1H); 7.9(*d*, CH-3, 1H) [ppm]

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