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Synthesis and Herbicidal Activities of *O*-Methyl *P*-(Dichloromethyl)phosphonamidates and Diamides†

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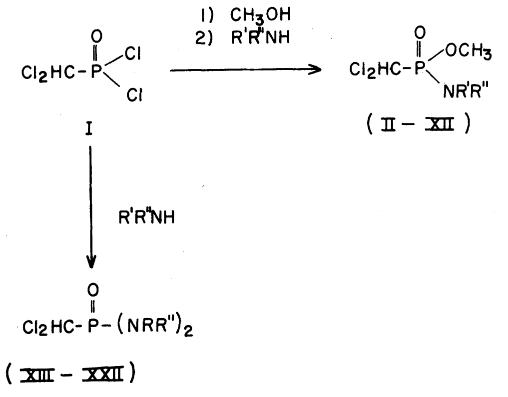
Eleven new *O*-methyl *P*-(dichloromethyl)phosphonamidates and ten corresponding diamides have been prepared and screened for their plant growth inhibitory and herbicidal activities. Structure activity relationships for both series of compounds are discussed.

Among the various types of organophosphorus compounds, some derivatives of phosphoramidic acid are known to possess harbicidal properties. The first organophosphorus herbicide introduced was DMPA (2,4-dichlorophenyl methyl *N*-isopropylphosphoramido thionate, Zytron). Recently, a few more such compounds have been developed into promising experimental herbicides.[1] It had been observed that variation of the *N*-alkyl group in phosphoramidates greatly influences their biological activity.[2] It was therefore of interest to discover this effect on the newer organophosphorus compounds. With this objective, a series of *O*-methyl *P*-(dichloromethyl)phosphonamidates and dichloromethylphosphonic diamides were synthesised by introducing different alkyl/aryl substituents (Scheme 1), and a systematic study of their plant growth regulatory and herbicidal properties was carried out. The preparation methods, physicochemical properties, growth regulatory and herbicidal activities of these are reported in this paper.



SCHEME 1.

EXPERIMENTAL

A. *Synthesis of compounds.* All melting points are uncorrected. The purity of the compounds was judged by the appearance of a single spot on thin layer chromatographic plates coated with silica gel G. The solvent system for the development of these plates was either an acetone–benzene (10 : 90) mixture (for *O*-methyl *P*-dichloromethylphosphonamidates) or an acetone–benzene (20 : 80) mixture (for the diamides). Iodine vapour was used as a visualizing agent. IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer and NMR spectra were on a 90 MHz model spectrometer using $CDCl_3$ as the solvent and TMS as an internal standard. Ammonia/gaseous amines were generated by gently heating their aqueous solutions and passing the resulting gas through calcium oxide.

O-methyl P-(dichloromethyl)phosphonamidates (**II ~ XII**). Dichloromethylphosphonic dichloride (I, 2.02 g, 0.01 mol), prepared according to the procedure of Roy and Mukerjee[3] and taken in dry methylene chloride (20 ml), was cooled to 0 ~ 5° and to this was added a solution of dry methanol (0.32 g, 0.01 mol) in methylene

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† Contribution No. 206.

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chloride (10 ml) dropwise with stirring. After the addition was complete, a slow but constant stream of dry amine/ammonia gas was bubbled through the solution until it was saturated. After standing for half an hour at room temperature, the inorganic salt was filtered off and the solvent removed by distillation. The residue after purification by column chromatography on silica gel, gave the product as a solid or oil. The solids were further recrystallized from a mixture of acetone and petroleum ether.

In the case of the liquid amines and anilines, a solution of the appropriate amine or aniline in methylene chloride was added dropwise with stirring just after the addition of methanol.

*Dichloromethylphosphonic diamides (***XIII**$\sim$**XXII***).* Dry amine or ammonia gas was passed through an ice cooled solution of dichloromethylphosphonic dichloride (2.02 g, 0.01 mol) in methylene chloride (25 ml) with stirring until saturation. The whole mixture was kept at room temperature for half an hour, the inorganic salt was filtered out and the solvent was distilled off. The residue was purified by column chromatography on silica gel to give the desired product. The physical and analytical data of *O*-methyl *P*-(dichloromethyl)phosphonamidates and diamides are listed in Tables I and II, respectively.

The IR spectra of the compounds of both these series showed conspicuous peaks at 1220$\sim$1250 cm^{-1} (P=O) and an additional peak at 960$\sim$970 cm^{-1} ($P\text{–}O\text{–}CH_3$) in the case of the phosphonamidates. Distinct adsorption bands in the ranges of 3150$\sim$3300 cm^{-1} (N–H) and 1100$\sim$1140 cm^{-1} (C–N) due to P–NH–R grouping[4] were observed. The NMR spectra of all these compounds showed a doublet at δ 5.8$\sim$5.9 (J_{P-H}=0.5 Hz to 1 Hz) due to the proton of the chloromethyl group. Two protons due to the NH_2 group appeared at δ 3.8 which slowly disappeared with the addition of D_2O. While the proton of the monosubstituted amide group ($N\underline{H}$–R) came as a broad hump between δ 4$\sim$6, methylene protons attached directly to the nitrogen atom appeared at δ 2.5$\sim$3 and subsequent methylene or methyl groups at δ 1$\sim$1.5. The aromatic protons (wherever present) appeared between δ 6.5$\sim$7. All

TABLE I. PHYSICAL AND ANALYTICAL DATA OF *O*-METHYL *P*-(DICHLOROMETHYL)PHOSPHONAMIDATES

Compound no.	Molecular formula	R′	R″	mp (°C)	Yield (%)	% Cl	
						Found	Calcd.
II	$C_2H_6O_2Cl_2PN$	H	H	120	60	39.4	39.9
III	$C_3H_8O_2Cl_2PN$	H	CH_3	Oil	45	37.3	37.0
IV	$C_4H_{10}O_2Cl_2PN$	H	C_2H_5	Oil	42	34.9	34.5
V	$C_5H_{12}O_2Cl_2PN$	H	C_3H_7	160	34	31.8	32.3
VI	$C_6H_{14}O_2Cl_2PN$	H	C_4H_9	172	45	29.9	30.3
VII	$C_5H_{12}O_2Cl_2PN$	H	$CH(CH_3)_2$	204$\sim$205	72	32.5	32.3
VIII	$C_8H_{10}O_2Cl_2PN$	H	C_6H_5	120	62	27.8	28.0
IX	$C_9H_{12}O_3Cl_2PN$	H	$C_6H_4OCH_3(p)$	132	70	25.0	25.0
X	$C_9H_{12}O_2Cl_2PN$	H	$C_6H_4\text{–}CH_3(p)$	161	49	26.9	26.5
XI	$C_4H_{10}O_2Cl_2PN$	CH_3	CH_3	141$\sim$142	58	34.1	34.5
XII	$C_6H_{14}O_2Cl_2PN$	C_2H_5	C_2H_5	158$\sim$160	60	30.0	30.3

TABLE II. PHYSICAL AND ANALYTICAL DATA OF DICHLOROMETHYLPHOSPHONIC DIAMIDES

Compound no.	Molecular formula	R′	R″	mp (°C)	Yield (%)	% Cl	
						Found	Calcd.
XIII	$CH_5N_2Cl_2OP$	H	H	Oil	50	43.6	43.5
XIV	$C_3H_9N_2Cl_2OP$	H	CH_3	Oil	42	36.9	37.2
XV	$C_5H_{13}N_2Cl_2OP$	H	C_2H_5	Oil	32	32.5	32.4
XVI	$C_7H_{17}N_2Cl_2OP$	H	C_3H_7	112	52	28.3	28.7
XVII	$C_9H_{21}N_2Cl_2OP$	H	C_4H_9	Oil	71	26.0	25.8
XVIII	$C_7H_{17}N_2Cl_2OP$	H	$-CH(CH_3)_2$	Oil	68	28.4	28.7
XIX	$C_{15}H_{17}N_2Cl_2O_3P$	H	$C_6H_4OCH_3(p)$	182$\sim$184	45	19.4	18.9
XX	$C_{15}H_{17}N_2Cl_2OP$	H	$C_6H_4\text{–}CH_3(p)$	190$\sim$192	69	20.3	20.7
XXI	$C_5H_{13}N_2Cl_2OP$	CH_3	CH_3	159$\sim$160	60	31.9	32.4
XXII	$C_9H_{21}N_2Cl_2OP$	C_2H_5	C_2H_5	124$\sim$126	54	26.2	25.8

the *O*-methyl *P*-dichloromethylphosphonamidates showed a conspicuous doublet at δ 3.9 ~ 4.1 ($J = 10 \sim 11$ Hz) due to methoxy protons.

B. *Biological screening.*

(i) *Pre-plantation studies.* The growth inhibitory activity of these compounds was studied by observing their effect on seed germination. As test plants, wheat (HD-2204 variety obtained from NSC, India) was chosen as the monocotyledonous representative and Mustard (*Brassica campastris*) for dicotyledonous plants. Solutions of these compounds were prepared in an acetone–water mixture (5 : 95). An emulsion was prepared by adding 0.2% Triton-X, for compounds insoluble in acetone. Five ml of these solutions, or suspensions containing 1000, 500, 250, 125 or 62.5 ppm of the test compound, was poured over a petri dish (9 cm diameter) covered with filter paper. Ten seeds of the test plant (wheat or mustard) were placed in each petri dish. Separate controls for the solutions (containing only acetone and water) and suspensions (containing Triton-X also) were kept. All the petri dishes were kept at room temperature for 7 days. One ml of distilled water was added after every 24 hr to maintain the moisture. Each test was triplicated. On the eighth day, the lengths of the roots and shoots of each germinated plant were measured. The average total length of the plant was compared with that

TABLE III. HERBICIDAL ACTIVITIES OF *O*-METHYL *P*-(DICHLOROMETHYL)PHOSPHONAMIDATES

Compound no.	50% growth inhibition (conc. in mg/litre)		Pre-emergence[a]		Post-emergence phytotoxicity[b]			
	Mustard	Wheat	Mustard	Wheat	Mustard	Wheat	Oat	Bottle gourd
II	200	340	3	3	B	A	B	B
III	220	340	2	3	A	B	A	B
IV	310	570	2	0	A	B	A	B
V	>1000	800	1	0	B	B	B	A
VI	95	250	4	4	C	B	B	C
VII	340	380	4	5	C	B	C	C
VIII	170	290	5	4	B	C	C	B
IX	140	180	4	3	D	C	B	D
X	290	310	3	4	B	B	C	C
XI	320	370	2	3	B	C	C	C
XII	500	420	3	4	C	B	B	C

[a] Rating for pre-emergence studies: 0, less than 50% inhibition at 1000 ppm; 1, more than 50% inhibition at 1000 ppm; 2, less than 50% inhibition at 500 ppm; 3, more than 50% inhibition at 500 ppm; 4, less than 50% inhibition at 100 ppm; 5, more than 50% inhibition at 100 ppm.

[b] Rating for post-emergence studies: A = no apparent effect; B = plant and leaves turn yellow initially but survive ultimately; C = the stem revived but the leaves were shed; D = complete kill.

TABLE IV. HERBICIDAL ACTIVITIES OF DICHLOROMETHYLPHOSPHONIC DIAMIDES

Compound no.	50% growth inhibition (conc. in mg/litre)		Pre-emergence[a]		Post-emergence phytotoxicity[b]			
	Mustard	Wheat	Mustard	Wheat	Mustard	Wheat	Oat	Bottle gourd
XIII	55	70	3	2	C	D	D	C
XIV	150	200	3	2	C	B	C	D
XV	300	280	1	3	B	C	B	C
XVI	310	350	3	1	B	A	B	B
XVII	450	360	3	4	C	B	B	C
XVIII	340	340	5	5	C	C	B	B
XIX	120	160	4	4	B	C	C	C
XX	210	280	4	3	C	B	B	C
XXI	320	350	3	4	B	A	B	B
XXII	340	380	3	2	A	A	B	A

[a,b] For ratings see the footnote of Table III.

in control and percentage inhibition of the plant growth calculated. This was plotted against the corresponding concentration. The concentrations in mg/litre required to inhibit 50% growth are recorded in the first two columns of Tables III and IV.

(ii) *Pre-emergence studies.* These were conducted in earthen ware pots (6″ height) filled with alluvial soil (obtained from the farms of IARI) which had previously been passed through a 2 mm sieve. The pots were adequately watered up to the proper water holding level. Five ml of the solution containing 1000, 500 or 100 ppm of the test chemicals was added. Ten seeds of the test plant (wheat or mustard) were sown separately in each pot and the pots were periodically watered. After 20 days, the crop was harvested with the help of a blade. The harvested material was dried in an air oven at 60°C for three hours. The weight of the dry matter was compared with that of control and the percentage inhibition was then calculated. The results presented in the third and fourth columns of Tables III and IV are based on six ratings. Compounds showing less than 50% inhibition at 1000 ppm are rated as 0 and more than 50% inhibition as 1. Similarly those showing less than 50% inhibition and more than 50% inhibition at 500 and 100 ppm have been rated as 2,3 and 4,5 respectively.

(iii) *Post emergence phytotoxicity.* Apart from wheat and mustard, two more crops, oat (*Avena sativa* kent) and bottle gourd (*Lagenaria sicraria*) were chosen for pot studies. Ten seeds were sown in each earthen ware pot containing alluvial soil from the same lot. After germination, the population was thinned to seven plants in each pot and then allowed to grow until three leaves had appeared. All the plants in a pot were drenched once with a total of five ml of 1000 ppm solution of the test compound and the effects were observed for a further period of 15 days. Four ratings (A–D) have been made on the basis of visual observation and the results are recorded in the last four columns of Tables III and IV.

RESULTS AND DISCUSSION

The plant growth inhibition data of *O*-methyl *P*-(dichloromethyl)phosphonamidates indicate that with an increase in number of straight chain carbon atoms in the *N*-alkyl group, there is a decrease in activity down to *O*-methyl *N*-propyl-*P*-(dichloromethyl)phosphonamidate, which shows practically no activity up to 1000 ppm. this is contrary to the earlier observation[2)] that a bulkier *N*-alkyl group induces higher herbicidal activity. However, further stepping up by one more carbon atom, *i.e.*, *O*-methyl *N*-butyl-*P*-(dichloromethyl)phosphonamidate (**VI**), introduced considerably enhanced activity for mustard. If the aliphatic amino group is replaced by the aromatic one, there is not much increase in activity except for the *p*-methoxy substituted anilide (**IX**) which exhibits moderate activity for both wheat and mustard.

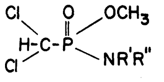

FIG. 1.

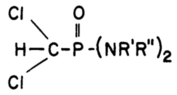

FIG. 2.

In the case of dichloromethylphosphonic diamides simple *P*-dichloromethylphosphonic diamide (**XIII**) was found to be the most active for both mustard and wheat. The activity decreases as the number of carbon atoms in the *N*-alkyl group increases, except in *p*-methoxy substituted anilide (**XIX**) which possesses moderate activity.

The pre-emergence phytotoxicity results on the series of phosphonamidates do not follow any systematic order of activity with an increase in the number of carbon atoms. However, branching of the carbon chain on the *N*-alkyl group, or its replacement by an aryl group, seems to enhance the activity. Thus, amongst the phosphonamidates, the isopropyl derivative (**VII**) and the simple anilide (**VIII**) are quite active for wheat and mustard respectively. In the series of diamides the most active compound is the isopropyl derivative (**XVIII**).

The results of the post-emergence phytotoxicity studies on the series of phosphonamidates show that the activities do not consistently increase or decrease with an increase of carbon atoms. The general observation was that the plant and the leaves turned yellow initially and survived ultimately with or without shedding the affected leaves. Complete kill was found in the case of *p*-methoxy substituted anilide (**IX**) for both mustard and bottle gourd. In the case of diamides, the simple phosphonamidate (**XIII**) and its methyl analogue (**XIV**) were found active; the former for wheat and oat and the latter for bottle gourd.

An analysis of Tables III and IV reveals that most of the compounds of both series exhibit activity to a similar extent in all the three tests against a particular crop with some exceptions. In the phosphonamidate series, the compounds **VII** and **VIII** possess good activity in the pre-emergence studies but these are not as active in the growth inhibition and post emergence studies where the compound **IX** was the most active. Similar observation is found in the case of the diamides, where the compound **XIII** is most active in the growth inhibition and post emergence phytotoxicity studies but shows poor activity under pre-emergence studies.

REFERENCES

1) M. Eto, "Organophosphorus Pesticides: Organic and Biological Chemistry," CRC Press Inc., Ohio, 1974, p. 325.
2) M. Aya, A. Fukazawa, S. Kishino and T. Kume, *Noyaku-kenkyu*, **17**, 169 (1968).
3) N. K. Roy and S. K. Mukerjee, *Ind. J. Chem.*, **10**, 1159 (1972).
4) L. C. Thomas, "Interpretation of Infra Red Spectra of Organophosphorus Compounds," Hyden, 1974, p. 116.