Synthesis and Fungicidal Activity of Diaryl 1,1-Dichloroethylphosphonates**

Diaryl 1,1-dichloroethylphosphonates (or phosphonodithioates) (III). A general procedure is given. A solution of 1,1-dichloroethylphosphonic dichloride (1 mol) in dry benzene was added dropwise with stirring to a cooled (10°C) solution of the substituted phenol (or thiophenol) (2 mol) in dry benzene containing dry triethylamine (2 mol). The reaction mixture was further stirred for 4 hr at room temperature. After filtering off the amine hydrochloride the solvent was removed by distillation and the residue was purified by recrystallisation from a mixture of pet, ether and benzene in the case of solids or by column chromatography over silica gel (coated with 1% oxalic acid) in the case of liquids where the distillation was unsuccessful. The physical and analytical data of the new phosphonates (or phosphonodithioates) (1–28) thus prepared are listed in Table I.

TABLE I. PHYSICAL ANALYTICAL DATA AND FUNGICIDAL ACTIVITY OF DIARYL 1,1-DICHLOROETHYL PHOSPHONATES (OR PHOSPHONODITHIOATES).

III

where X = O (Nos. 1–24); X = S (Nos. 25–28)

Structure III

No.	R	mp (°C)	Yield (%)	Cl (%)		ED ₅₀ (mg ml ⁻¹)			
				Found	Clacd	<i>P. oryzae</i>	<i>H. oryzae</i>	<i>A. alternata</i>	<i>R. bataticola</i>
1	H	66	70	21.2	21.4	0.60	0.70	0.90	NA ^a
2	4-Cl	48	75	35.8	35.5	1.0	1.0	1.0	NA
3	2-Cl	55	72	35.1	35.5	1.0	1.0	1.0	NA
4	4-NO ₂	123	80	16.6	16.9	0.50	0.80	0.80	0.80
5	3-NO ₂	106	78	17.0	16.9	0.70	0.90	1.0	0.90
6	2-NO ₂	72	79	16.7	16.9	0.50	0.80	0.70	1.0
7	4-CH ₃	Liquid ^b	70	20.0	19.8	1.0	0.50	0.80	1.0
8	3-CH ₃	Liquid ^b	68	19.5	19.8	0.90	0.50	1.0	1.0
9	2-CH ₃	Liquid ^b	70	19.9	19.8	0.60	0.50	0.80	0.80
10	4-OCH ₃	72	73	18.4	18.1	1.0	NA	1.0	NA
11	2-OCH ₃	Liquid ^b	68	18.3	18.1	1.0	1.0	1.0	1.0
12	4- <i>t</i> -C ₄ H ₉	105	70	15.8	16.0	NA	NA	NA	NA
13	4-SCH ₃	75	80	16.5	16.8	1.0	1.0	1.0	1.0
14	2-NO ₂ , 5-CH ₃	114	78	15.5	15.8	1.0	1.0	0.6	NA
15	3-CH ₃ , 4-Cl	Liquid ^b	70	33.4	33.2	0.80	0.40	0.25	1.0
16	2-Cl, 4-NO ₂	148	78	28.8	29.0	0.07	0.08	0.20	0.08
17	2,4-Cl ₂	Liquid ^b	72	45.0	45.4	0.10	0.10	0.15	0.15
18	3-CH ₃ , 4-SCH ₃	60	75	15.4	15.7	NA	NA	NA	NA
19	2,4,5-Cl ₃	108	77	52.6	52.8	0.02	0.08	0.06	0.04
20	2,4-Me ₂	Liquid ^b	66	18.1	18.3	0.80	0.70	0.50	1.0
21	2,6-Me ₂	Liquid ^b	65	17.9	18.3	1.0	1.0	0.90	NA
22	3,4-Me ₂	Liquid ^b	67	18.5	18.3	NA	0.60	0.60	NA
23	3,5-Me ₂	Liquid ^b	62	17.9	18.3	NA	NA	NA	NA
24	2,3-Me ₂	Liquid	65	18.0	18.3	NA	0.80	0.90	NA
25	H	88	73	19.2	19.5	0.70	0.40	0.35	0.50
26	4-Cl	103	70	33.0	32.9	0.90	1.0	0.60	NA
27	4-Br	129	72	13.3	13.6	0.80	1.0	0.80	NA
28	4-Me	87	70	18.0	18.1	1.0	1.0	0.80	NA

^c*O,O*-Di(2,4,5-trichlorophenyl)dichloromethyl phosphonate (for comparison)

0.003 0.02 0.04 0.03

^a NA, not active upto 1 mg ml⁻¹, ^b column purified, ^c unpublished data.

Fungicidal activity. The fungicidal efficacy of the phosphonates (or *Phosphonodithioates*) against *Pyricularia oryzae* cav., *Helminthosporium oryzae* Auct., *Alternaria alternata* Breda de Haan and *Rhizoctonia bataticola* (Tassi) Goid was carried out by the poisoned food technique using standard potato-dextrose agar as described by Nene and Thapliyal.⁵⁾ ED₅₀ values were determined from the data for 5 concentrations on a log probit scale and are presented in Table I.

RESULTS AND DISCUSSION

Table I shows that the fungi toxicity of the phosphonates and phosphonodithioates against *P. oryzae*, *H. oryzae*, *A. alternata* and *R. bataticola* is not dependent on the electronic nature of the substituents in the benzene ring. The simple phenyl analogue has poor activity against all the test fungus. The degree of activity remains more or less static when the benzene ring is substituted by nitro and methyl groups. Other substituent like chlorine, methoxy, thiomethyl, tertiary butyl group make the phosphonates poorer in activity. The degree of activity of the phos-

phonates has been enhanced in few cases after the introduction of the second substituent in the benzene ring. This is evident from the data of compound Nos. 16 and 17. The most active compound in this series against all the test fungus is *O,O*-di (2,4,5-trichlorophenyl) 1,1-dichloroethylphosphonate. Even this compound is poorer in activity in comparison to *O,O*-di (2,4-5-trichlorophenyl) dichloromethylphosphonate (taken as standard).*

The phosphonodithioates are found to possess the same degree of activity as their phosphonate analogues. Hence, it can be concluded that the degree of activity has been reduced by lengthening the carbon chain by one carbon atom.

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REFERENCES

- 1) M. Eto, "Organophosphorus Pesticides, Organic and Biological Chemistry," CRC Press, USA, 1974, p. 312.
- 2) S. Bedi and N. K. Roy, *Indian J. Agr. Sci.*, **48**(4), 248 (1978).
- 3) N. K. Roy and S. K. Mukerjee, *Pestic Sci.*, **6**, 497 (1975).
- 4) L. M. Jackman and S. Sternhell, "Application of NMR Spectroscopy in Organic Chemistry," Pergamon Press, USA, 1969, p. 351.
- 5) Y. L. Nene and P. N. Thapliyal, "Fungicides in Plant Disease Control," 2nd Ed., Oxford & IBH Publishing Co., New Delhi, 1979, p. 413.

* Unpublished data.