

Table III. Recovery of Isopropyl N-(3-Chlorophenyl)carbamate

CIPC Added		Transmittance, %, 540 m μ	CIPC Found			
Mg.	P.p.m.		Total		Net	
			Mg.	P.p.m.	P.p.m.	% Recovery
MILK (100-GRAM SAMPLES)						
0.000	0.000	67	0.0072	0.072
	0.000	70	0.0063	0.063
	0.000	66.5	0.0073	0.073
0.010	0.000	70	0.0063	0.063
	0.100	45	0.0155	0.155	0.087	87
	0.100	48	0.0142	0.142	0.074	74
	0.100	51	0.0130	0.130	0.062	62
	0.100	42	0.0170	0.170	0.102	102
	0.100	47	0.0147	0.147	0.079	79
					Av.	81
URINE (200-GRAM SAMPLES)						
0.000	0.000	78	0.0040	0.020
	0.000	76	0.0047	0.024
	0.000	76.5	0.0044	0.022
	0.000	79	0.0038	0.019
0.005	0.025	65	0.0080	0.040	0.019	76
	0.025	64	0.0084	0.042	0.021	84
	0.025	66.5	0.0073	0.037	0.016	64
	0.025	63.5	0.0085	0.043	0.022	88
	0.025	68	0.0070	0.035	0.014	56
					Av.	74

some components which respond to the analytical methods and thus cause interference. The calculated average interference for the milk samples is 0.068 p.p.m. expressed as CIPC; and for urine is 0.021 p.p.m. The precision of the methods based on 95% confidence limits is $\pm 19.91/\sqrt{n}\%$ of the average

of n determinations. This precision applies to levels ranging from 0.02 to 0.15 p.p.m. of CIPC. The calculated average recovery of CIPC from the samples of milk fortified at the 0.1 p.p.m. concentration level in the laboratory is 81%. Similarly, samples of aged urine fortified at the 0.025 p.p.m.

concentration level gave a calculated average recovery of 74%.

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INSECTICIDE SCREENING

Synthesis and Insecticidal Activity of O-Methyl O-(2,4,5-Trichlorophenyl) Phosphoramidothioates and Related Compounds

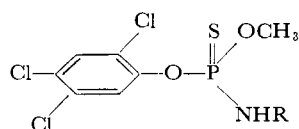
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PRACTICALLY all the work reported on the synthesis and biological activity (7, 10) of organic phosphorus compounds has been done on triesters containing two methyl groups or two ethyl groups. The investigations described in this publication are concerned with the synthesis and insecticidal activity of a series of O-methyl O-(2,4,5-trichlorophenyl) phosphoramidothioates,



where R is hydrogen or an aliphatic

hydrocarbon radical containing one to four carbon atoms.

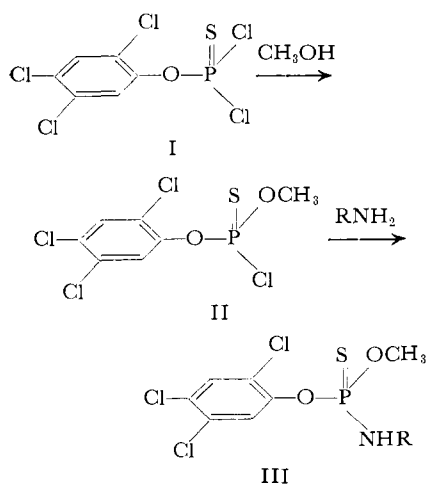
Different phosphorus acid chlorides can be used to prepare O-alkyl O-aryl phosphoramidothioates. Alkylphosphoramidodichloridothioates (9), O-alkyl phosphorodichloridothioates (6, 9), and O-aryl phosphorodichloridothioates (4, 6) have been used for such purposes. The dichloridothioates are converted to monochloridothioates by esterification with an alcohol or a phenol in the presence of hydrogen chloride acceptors. However, the purity and yields of many of these intermediates as well as the final products have not been entirely satisfactory due to the

formation of other phosphorus derivatives. An improved method for the preparation of various thiophosphoric acid chlorides was therefore desirable.

Chemical Studies

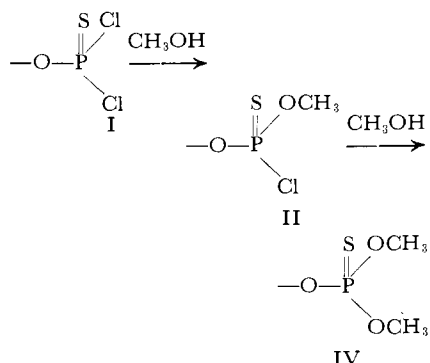
O-(2,4,5-Trichlorophenyl) phosphorodichloridothioate (I), available in high purity (12), appeared to be an ideal starting material. Since the authors were interested in preparing O-alkyl O-aryl phosphoramidothioates in which the two ester groups were constant constituents(III), O-methyl O-(2,4,5-trichlorophenyl) phosphorochloridothioate (II) was prepared for use as an intermediate (13).

The synthesis, physical properties, and insect toxicities of a series of *O*-methyl *O*-(2,4,5-trichlorophenyl) phosphoramidothioates are described. The amidothiophosphate esters were prepared by amidation of *O*-methyl *O*-(2,4,5-trichlorophenyl) phosphorochloridothioate. The latter compound was obtained as a crystalline intermediate by partial esterification of *O*-(2,4,5-trichlorophenyl) phosphorodichloridothioate with methanol in the absence of a hydrogen chloride acceptor. The results of the insecticide tests show that the *O*-methyl *O*-(2,4,5-trichlorophenyl) phosphoramidothioates have a wide spectrum of toxicity and are residually toxic when houseflies are exposed to treated panels.



Inasmuch as hydrogen chloride, a by-product in the methanolysis of the dichloridothioate (I), may give undesirable side reactions, removal or neutralization of the acid was desirable. A satisfactory procedure was to add a large excess of methanol to the dichloridothioate (I) and remove the hydrogen chloride by codistillation with methanol during the reaction. The amount of hydrogen chloride liberated was equivalent to only one chlorine atom of the phosphorodichloridothioate (I). Thus, it is evident that the chlorine atom of *O*-methyl *O*-(2,4,5-trichlorophenyl) phosphorochloridothioate (II) is displaced with more difficulty than one of the chlorine atoms of the dichloridothioate (I).

Esterification of *O*-(2,4,5-trichlorophenyl) phosphorodichloridothioate with methanol probably proceeds via two consecutive bimolecular reactions:



In the reaction I \rightarrow II \rightarrow IV, the phosphorus atom of the dichloridothioate (I) is more susceptible to nucleophilic attack than the phosphorus atom of the monochloridothioate (II). The methoxyl group resulting from displacement of one of the chlorine atoms decreases the positive charge on phosphorus by an inductive effect. The resulting increase in electron density about the phosphorus atom causes the remaining chlorine atom to be less susceptible to nucleophilic displacement. Bimolecular mechanisms have been reported for the solvolysis reactions of aryl phosphorodichloridates with methanol (11) and for the reactions of *O*-aryl phosphorodichloridothioates with amines (2, 14).

O-Methyl *O*-(2,4,5-trichlorophenyl) phosphorochloridothioate was obtained as a crystalline compound in high yield (13). It is soluble in most organic solvents and insoluble in water. It is relatively stable to hydrolysis and can be amidated in aqueous systems. When stored at room temperature for long periods of time, the compound deteriorated and developed bad odors. It was, however, stored at 10° C. for years with no apparent decomposition.

O-Methyl *O*-(2,4,5-trichlorophenyl) phosphoramidothioates were prepared by dissolving recrystallized *O*-methyl *O*-(2,4,5-trichlorophenyl) phosphorochloridothioate in a suitable solvent and adding at least two equivalents of an aqueous (7) or anhydrous amine. In accordance with previous observations (2, 5), a decrease in the rate of amide formation was noted in progressing from anhydrous ammonia and primary amines to the branched and bulkier amines. The phosphoramidothioates were crystalline solids with well-defined melting points. Many of the crude products were obtained in the crystalline state by removing solvent and allowing to stand or by pouring into water. The ease of crystallization was due to the purity of the starting materials and intermediates. The amides are soluble in most organic solvents and insoluble in water. They appeared to be relatively stable to

base hydrolysis but were hydrolyzed by strong inorganic acids. The physical properties and analytical data of the *O*-methyl *O*-(2,4,5-trichlorophenyl) phosphoramidothioates are listed in Table I.

Two commercial products (Zytron pesticide, trademark of The Dow Chemical Co., and Ronnel, trademark of The Dow Chemical Co. abroad) used for comparative insecticidal purposes have groupings common to the above *O*-methyl *O*-(2,4,5-trichlorophenyl) phosphoramidothioates. Zytron, *O*-(2,4-dichlorophenyl) *O*-methyl isopropylphosphoramidothioate (9), was synthesized from *O*-(2,4-dichlorophenyl) phosphorodichloridothioate by the method discussed above. Ronnel, *O,O*-dimethyl *O*-(2,4,5-trichlorophenyl) phosphorothioate (8), was prepared by treating *O*-methyl *O*-(2,4,5-trichlorophenyl) phosphorochloridothioate with methanol and sodium hydroxide (3). Both compounds were recrystallized to constant melting points.

Synthesis

The *O*-aryl phosphorodichloridothioates used have been previously described (12). The liquid organic amines employed were freshly redistilled commercial products. Gaseous amines were volatilized into a chilled flask, then used. Melting points were determined on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. The synthetic procedures for the preparation of the various amidothiophosphates are illustrated by the following examples.

***O*-Methyl *O*-(2,4,5-Trichlorophenyl) Phosphorochloridothioate.** Four liters of methanol was added over a period of 7.0 hours to 400.0 grams (1.21 moles) of *O*-(2,4,5-trichlorophenyl) phosphorodichloridothioate. The addition was carried out at a rate of approximately 550 ml. per hour with stirring at a pressure of 193 mm. and a temperature of 42° to 49° C. During the alcohol addition, a methanol-hydrogen chloride solution continuously distilled from the reaction flask. The solution was titrated each hour to determine the progress

of the reaction. After 7.0 hours, the evolution of hydrogen chloride was substantially complete. A total of 1.21 moles of hydrogen chloride was evolved. The reaction mixture was placed under 20 mm. pressure, and the temperature of the mixture was raised to 55° C. and held for 15 minutes to remove final traces of methanol and acid. The product solidified when cooled, m.p. 35° to 38° C., yield 90% (353.0 grams).

An analytical sample, m.p. 37° to 38° C. was obtained by recrystallization from petroleum ether (b.p. 30° to 60° C.).

ANALYSIS. Calcd. for C₇H₃Cl₃O₃PS: Cl, 43.51; S, 9.82. Found: Cl, 43.05; S, 9.81.

O-Methyl O-(2,4,5-Trichlorophenyl) Phosphoramidothioate. Fifty grams of 20% aqueous ammonia was added dropwise in 30 minutes to an agitated solution of 0.224 mole (79.0 grams) of O-methyl O-(2,4,5-trichlorophenyl) phosphorochloridothioate in 225 ml. of acetone cooled to 15° C. The reaction mixture was stirred at room temperature for 30 minutes. The addition of 250 ml. of water caused the product to separate as an oil. The oil was collected and washed twice with 100 ml. of water. On the final wash, the mixture was cooled to bring about solidification of the product. After standing overnight, the product was filtered and dried. A nearly quantitative yield was obtained, m.p. 66° to 67° C. Recrystallization from methyl cyclohexane gave 55.0 grams of colorless crystalline amide, m.p. 66° to 67° C.

O-Methyl O-(2,4,5-Trichlorophenyl) Methylphosphoramidothioate. To 0.25 mole (81.5 grams) of O-methyl O-(2,4,5-trichlorophenyl) phosphorochloridothioate dissolved in 200 ml. of methylene chloride was added, in 0.5 hour, 0.625 mole (20.0 grams) of gaseous methylamine. External cooling was necessary to keep the temperature at 15° to 25° C. After the reaction mixture was stirred at room temperature for 0.5 hour, 200 ml. of water was added to dissolve methylamine hydrochloride. The organic phase was separated and washed two additional times with water. After distilling the solvent under reduced pressure, a liquid product remained. This solidified when poured into ice water. The product was filtered and dried, m.p. 42.5° to 43.5° C., yield 83%. An analytical sample was obtained by recrystallizing from isopropyl alcohol, m.p. 42.5° to 43.5° C.

O-Methyl O-(2,4-Dichlorophenyl) Isopropylphosphoramidothioate. O-methyl O-(2,4-dichlorophenyl) phosphorochloridothioate was prepared by the methanolysis of O-(2,4-dichlorophenyl) phosphorodichloridothioate in the identical manner reported for the preparation of O-methyl O-(2,4,5-tri-

Table I. Physical and Analytical Data of O-Methyl O-(2,4,5-Trichlorophenyl) Phosphoramidothioates

R ^a	Yield, % ^b	M.P., ° C.	Recrystallization Solvent	Nitrogen, %		Chlorine, %	
				Calcd.	Found	Calcd.	Found
—H ^c	98.0	66–67	Methylcyclohexane	4.57	4.39	34.70	34.77
—CH ₃	83.0 ^d	42.5–43.5	Isopropyl alcohol	4.37	4.35	33.18	33.02
—C ₂ H ₅	90.5	42–43	Petroleum ether ^e	4.18	4.07	31.78	32.22
—C ₃ H ₇	80.0	21–22 ^f	Petroleum ether ^e	4.02	4.01	30.59	30.35
—CH(CH ₃) ₂	88.5	73–74	Petroleum ether ^g	4.02	3.98	30.59	30.17
—C ₄ H ₉	81	36–37	Petroleum ether ^e	3.86	3.42	29.33	29.20
—CH(CH ₃)C ₂ H ₅	63.5 ^d	39–40	Petroleum ether ^e	3.86	3.90	29.33	29.26
—CH ₂ CH(CH ₃) ₂	87.0	35–36	Petroleum ether ^e	3.86	3.78	29.33	29.72
—C(CH ₃) ₃	95.5	104–105	Methylcyclohexane	3.86	4.01	29.33	28.85

^a From anhydrous amines. ^b Yield of technical grade material. ^c From 20% aqueous ammonia. ^d Yield of purified product. ^e (B.p. 30° to 60° C.). ^f *d*₄²⁵ 1.3820, *n*_D²⁵ 1.5648. ^g (B.p. 60° to 70° C.).

chlorophenyl) phosphorochloridothioate. It was obtained as a viscous liquid. Three hundred milliliters of methylene chloride containing 0.475 mole (138.5 grams) of the acid chloride was cooled to 7° C. and treated with 1.015 mole (60 grams) of isopropylamine. The addition was completed in 0.5 hour. During this time, the temperature of the reaction mixture increased to 17° C. After being stirred for 2 hours at room temperature, the reaction mixture was washed twice with 500-ml. portions of water. After removal of the solvent by distillation, 140.0 grams (94% yield) of product was obtained as a pale yellow oil which solidified on standing. The amide was recrystallized twice from methanol at -20° C. and once from petroleum ether (b.p. 30° to 60° C.) at 0° C., to give a colorless solid, m.p. 51° to 52° C.

ANALYSIS. Calcd. for C₁₀H₁₄Cl₂NO₂PS: Cl, 22.55; N, 4.46; S, 10.21; P, 9.86. Found: Cl, 23.05; N, 4.40; S, 10.20; P, 9.80.

O,O-Dimethyl O-(2,4,5-Trichlorophenyl) Phosphorothioate. O-methyl O-(2,4,5-trichlorophenyl) phosphorochloridothioate (0.5 mole, 163.0 grams) was dissolved in 800 ml. of methanol and cooled to -4° C. Three hundred milliliters of methanol containing 0.5 mole (20 grams) of sodium hydroxide was slowly added over a period of 80 minutes. During the addition, the reaction mixture was rapidly stirred, and the temperature was maintained at 0° to -4° C. After warming to room temperature, excess methanol was removed by distillation under reduced pressure. To the resulting semisolid was added 800 ml. of ice and water containing 10 ml. of acetic acid. The product immediately solidified, and was filtered, washed with

water, and air dried to give 150 grams of product, m.p. 14° to 42° C., yield 93.5%. After recrystallization from petroleum ether (b.p. 60° to 70° C.), the ester melted at 41.5° to 42° C.

ANALYSIS. Calcd. for C₈H₈Cl₃O₃PS: Cl, 33.08; S, 9.97; C, 29.87. Found: Cl, 32.74; S, 10.36; C, 29.85.

Insecticide Testing Procedures

Insecticide Screening Tests. Tests with agricultural insects were accomplished by use of the following insects and methods. Primary leaves of Cranberry bean plants, *Phaseolus vulgaris* L. (var. Cran.), were dipped in aqueous dilutions containing thiophosphates. The leaves when dry were infested with third instar larvae of the Mexican bean beetle, *Epilachna varivestis* Muls., or third instar larvae of the southern army worm, *Prodenia eridania* (Cram.). Cranberry bean plants and dwarf nasturtium plants, *Tropaeolum minus* L., previously infested with adults of the two-spotted spider mite, *Tetranychus telarius* L., and adults and nymphs of the bean aphid, *Aphis fabae* Scop., respectively, were dipped in the same dilution.

Mexican bean beetles, two-spotted spider mites, and southern army worms were held for 6 days and bean aphids for 3 days post-treatment before making mortality counts.

The plum curculio, *Conotrachelus nenuphar* (Herbst), was tested by placing five adults, 3 to 30 days old, into a perforated paper soufflé cup containing a small green apple. The insecticidal dilution was poured into the cup, thus immersing the insects and apple simultaneously. Excess material was drawn from the cup by suction through bottom perforations. The treated cup

Table II. Insecticidal Activity of O-Methyl O-(2,4,5-Trichlorophenyl) Phosphoramidothioates and Two Related Thiophosphates

R	Screening Tests (Insect Species ^a , LD ₅₀ , p.p.m.)								Topical Tests, (Gammas per Female Housefly)	
	SAW	MBB	PC	2SSM	BA	AR	HF	CFB	LD ₅₀	LD ₉₅
—H	150	180	28	40	12	105	12	500	0.05	0.10
—CH ₃	270	80	55	27	40	100	9	330	0.12	0.21
—C ₂ H ₅	200	110	70	20	25	40	6	350	0.07	0.10
—C ₃ H ₇	500	200	19	45	220	150	37	500	0.15	0.23
—CH(CH ₃) ₂	200	150	17	12	13	22	3.6	500	0.10	0.20
—C ₄ H ₉	500	200	70	80	300	300	100	500	0.23	0.57
—CH(CH ₃)C ₂ H ₅	500	190	110	220	500	18	18	25	0.33	0.42
—CH ₂ CH(CH ₃) ₂	500	160	110	95	220	120	80	220	0.35	0.53
—C(CH ₃) ₃	220	200	16	6	500	150	7	1.5	0.83	1.75
Ronnel	115	170	35	230	2.5	100	3	140	0.04	0.10
Zytron	540	350	70	150	380	110	4	500	0.11	0.24

^a SAW, southern army worm; MBB, Mexican bean beetle; PC, plum curculio; 2SSM two-spotted spider mite; BA, bean aphid; AR, American cockroach; HF, housefly; CFB, confused flour beetle.

was then covered with a fine mesh screen cap and held for 6 days before mortality counts were taken.

Household and stored grain insect tests were conducted in plastic-lined, paper cylinder containers. A tight-fitting, stainless steel band was slipped over the bottom of the cylinder to hold a filter paper in place. The top of the cylinder was fitted with a screened ring. Twenty-five each of the following insect species were placed in each container: 5-week-old nymphs of the American cockroach, *Periplaneta americana* L.; mixed male and female houseflies, *Musca domestica* L., adults, 4 days old; and 1-month-old adults of the confused flour beetle, *Tribolium confusum* Duv. The insecticidal dispersion was poured over the anesthetized insects in the container, thoroughly wetting them by immersion. The excess liquid was then drawn through the filter paper in a Büchner funnel by suction. The treated insects were held for three days at 80° F. in this container before mortality counts were made.

The LD₅₀ as extrapolated from data plotted on logarithmic-probability paper for various insects and arthropods are given in Table II.

Topical Evaluation Tests. For a more critical insecticidal evaluation, a microdrop applicator was used to measure and apply exact amounts of chemical to each insect. This applicator consists of a controlled piston which delivers a precise volume of an acetone solution through a detachable capillary tube and hypodermic needle and deposits the microdrop onto the dorsal surface of the thorax of each insect.

Three-day-old female houseflies were used as the test insects. The insects, immobilized by cold temperature (28°

to 36° F.), were selected, and 25 were treated and placed in the previously described type of household insect cage. A 2- μ l. drop was applied to each housefly. After treatment, the insects were held for 24 hours in a room having a constant temperature of 80° F. and a relative humidity of 60%. Mortality counts were then made.

Results of these tests were plotted on logarithmic-probability scale paper. A line was drawn to fit the plotted dosage mortality points from which the LD₅₀ and LD₉₅ points were taken for each insecticide on each insect species.

The results of these tests and those with Ronnel, lindane, malathion, and Zytron are shown in Table II.

Housefly Residual Panel Test. The object of this test was to determine how long a chemically treated, unpainted wooden surface will remain insecticidally active when infested with untreated housefly adults at weekly intervals following treatment. A 0.25-inch thick fir plywood panel, 6 inches square, was treated by pipetting an acetone solution of the insecticide evenly on both sides of the panel. The treated panel was hung from the top center of a 1-foot cubical screen cage. Food and water were placed in the bottom of the cage. One hundred 3-day-old flies were released in each cage and held in a room at 80° F. Mortality counts were taken 24 hours after infestation (Table III).

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Table III. Residual Insecticidal Effectiveness of Wooden Panels Treated with O-Methyl O-(2,4,5-Trichlorophenyl) Phosphoramidothioates and Some Commercial Pesticides on the Housefly

R	Mg. Sq. Ft.	No. of Days Over	
		70% Mortality	95% Mortality
—H	40	77	28
	20	1	1
—CH ₃	40	91	49
	20	0	0
—C ₂ H ₅	40	63	49
	20	21	0
	10	0	0
—CH(CH ₃) ₂	40	75	75
	20	35	30
	10	30	14
—CH(CH ₃)C ₂ H ₅	40	21	1
Ronnel	40	33	25
	20	20	20
	10	14	14
Zytron	40	91	42
	20	14	1
	10	1	1
Lindane	40	42	28
	20	42	21
	10	21	7
Malathion	40	7	1
	20	1	0

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