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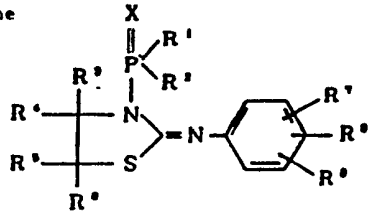
(54) Organophosphorus compounds having pesticidal activity, their preparation and use

(57)

Compounds of the formula:



(I)

wherein R^1 and R^2 each represent C_1–C_5 alkylthio, R^3, R^4, R^5 and R^6 each represent hydrogen or C_1–C_5 alkyl, R^7, R^8 and R^9 each represent hydrogen, C_1–C_5 alkyl or halogen, and X represents oxygen or sulfur, have pesticidal activity.

GB 2 184 123 A

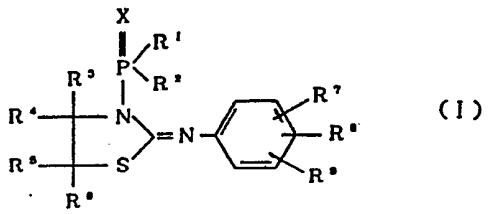
SPECIFICATION

Organophosphorus compounds having pesticidal activity, their preparation and use

This invention relates to novel organophosphorus compounds having pesticidal activity. More particularly, it relates to novel organophosphorus compounds containing a thiazolidine ring, to their preparation and to pesticidal compositions containing the novel compounds.

Although a wide variety of pesticides have been put to practical use, more efficient and less toxic pesticides have continuously been sought.

The present inventors previously found that a series of phosphonic acids exhibited an excellent pesticidal activity (see British Patent Specification 2,166,442 A and Japanese Patent Application 170507/1985). During an extended study on organophosphorus compounds, it has now been found that organophosphorus compounds of the formula:

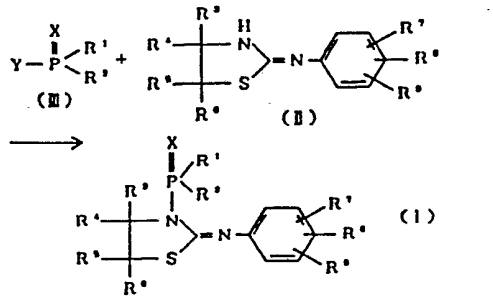


(I)

wherein R^1 and R^2 each represent C_1–C_5 alkoxy or C_1–C_5 alkylthio, R^3, R^4, R^5 and R^6 each represent hydrogen or C_1–C_5 alkyl, R^7, R^8 and R^9 each represent hydrogen, C_1–C_5 alkyl or halogen, and X represents oxygen or sulfur, exhibit an excellent pesticidal activity towards various pests, particularly towards spider mites which show resistance to known pesticides.

The term "pests" used herein should be considered to include insects and mites harmful to plants, especially phytophagous ones, and, the term "pesticides" or "pesticidal composition" to include insecticides and acaricides.

The compounds of the invention may be prepared according to the following reaction scheme:



(II) (III) (I)

wherein Y represents a leaving group, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and X are as defined above.

The term "C_1–C_5 alkyl" herein used includes straight or branched saturated hydrocarbon radical having one to five carbon atoms, including methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, tert-pentyl, neopentyl, 1-methylbutyl, 1,2-dimethylpropyl, and the like.

The term "C_1–C_5 alkoxyl" includes C_1–C_5 alkyl attached to a divalent oxygen atom and includes methoxy, ethoxy, propoxy, isopropoxy, butoxy, pentyloxy, and the like.

The term "C_1–C_5 alkylthio" includes C_1–C_5 alkyl attached to a divalent sulfur atom and includes methylthio, ethylthio, propylthio, isopropylthio, butylthio, pentylthio, and the like.

The term "halogen" means chloro, bromo, iodo or fluoro.

The term "leaving group" means any group which is readily removed from the moiety to which it has been attached. Such leaving groups are exemplified by chloro, bromo, iodo, or other acid residues.

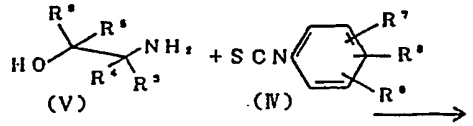
As previously stated, the compounds (I) may be prepared by the reaction between compounds (II) and compounds (III). The reaction is preferably conducted in an appropriate inert solvent although the use of solvent is not essential. Appropriate solvents include aliphatic hydrocarbons such as n-hexane and cyclohexane, aromatic hydrocarbons such as benzene, toluene and xylene, ketones such as acetone and methyl isobutyl ketone, ethers such as ethyl ether, tetrahydrofuran and dioxane, and halogenohydrocarbons such as dichloromethane and chlorobenzene. In addition, the reaction is conveniently carried out in the presence of an acid scavenger such as aliphatic

tertiary amines (e.g. trimethylamine, triethylamine, tributylamine), aromatic amines (e.g. dimethylaniline, diethylaniline), heterocyclic amines (e.g. pyridine, α-picoline, γ-picoline), and inorganic bases (e.g. sodium carbonate, potassium carbonate).

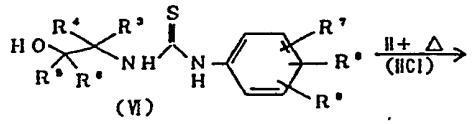
The reaction temperature is usually from 0°C to 100°C, preferably from 20°C to 80°C. The reaction time is usually from one to twelve hours with the preferred time being from two to eight hours.

The reaction product may be isolated and purified by conventional procedures such as extraction, recrystallization, column chromatography, etc.

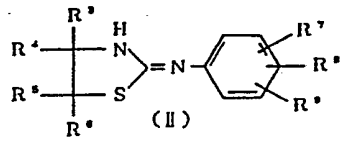
The starting materials used in the present invention may be prepared according to the following reaction schemes:



(V) (IV)



(VI)



(II)

wherein R^3, R^4, R^5, R^6, R^7, R^8 and R^9 are as previously defined.

An aryl isothiocyanate of the formula (IV) is allowed to react with an ethanolamine derivative of the formula (V) to obtain an N-hydroxyethylthiourea compound of the formula (VI), which may then be heated at temperature between 100 and 110°C in the presence of an acid catalyst such as hydrochloric acid to give the desired starting compound (II). In this reaction, 1.0 to 1.2 mole equivalents of the ethanolamine (V) and 2.0 to 10.0 mole equivalents of the acid catalyst are preferably employed reactive to one mole equivalent of the aryl isothiocyanate (IV).

The compounds of formula (I) of the present invention exhibit excellent pesticidal activity against phytophagous pests of various orders, such as Acarina, Orthoptera, Heteroptera, Lepidoptera, Diptera and Coleoptera. Therefore, the present invention also provides a pesticidal formulation or composition which comprises as an active ingredient a compound of formula (I) optionally together with a suitable carrier and/or adjuvant. The pesticidal compositions of the invention may be in any desirable form, such as dusts, granules, wettable powders, emulsifable concentrates, suspensions, aerosols, flowables, etc., and may be prepared by standard procedures. Solid carriers employable in the preparation of the pesticidal compositions of the invention include vegetative flour such as corn, soybean or wheat flour, mineral powder such as clay, bentonite, terra abla, vermiculite, talc, diatomaceous earth, pumice or active carbon, synthetic resins such as vinyl chloride or polystyrene. Illustrative liquid carriers are hydrocarbons such as kerosene, solvent naphtha, toluene and xylenes, alcohols such as methanol, ethanol, ethylene glycol and polypropylene glycol, ethers such as dioxane and cellosolve, ketones such as methyl isobutyl ketone and cyclohexanone, halogenated hydrocarbons such as dichloroethane and trichloroethane, esters such as dioctyl phthalate, amides such as dimethylformamide, nitriles such as acetonitrile, fats and oils water, and the like.

The adjuvants employed in the preparation of the pesticidal compositions of the invention include surfactants, wetting agents, sealing agents, thickening agents, stabilizing agents, etc. Specific examples of the adjuvants are anion surfactants such as alkylsulfonates, lignin sulfonates and alkyl sulfates, nonionic surfactants such as alkylpolyoxyethylene ethers, sorbitan esters, polyoxyethylene fatty acid esters and sucrose esters, water-soluble polymers such as casein, gelatin, carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), gum arabic and alginic acid.

The compositions of the invention may contain, if desired, one or more other insecticides, bactericides, herbicides, soil conditioners and fertilizers.

The pesticidal compositions of the invention preferably contain as an active ingredient 0.1 to 99.9%, preferably about 2 to 80% by weight of the compound (I). With a wettable powder or emulsifiable concentrate, the preferred content of the active ingredient ranges from 10 to 50% by weight.

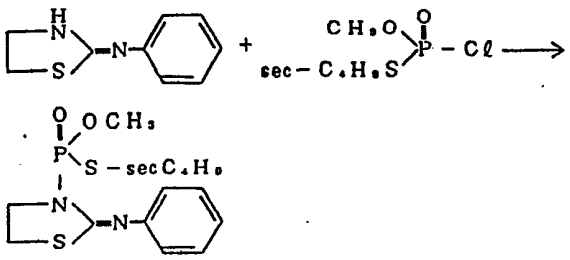
The amount of the present formulations or compositions to be applied to the loci of phytophagous pests will vary depending on a number of factors, such as an application method, season or locus of application, species of pests and crops, and the like. However, the compositions are usually applied at an application rate of 200 to 600 liter per 10 are, after being diluted 500 to 10,000 fold, preferably 1,000 to 5,000 fold.

Dust compositions of the present invention usually contain from 0.5 to 10%, preferably from 2 to 5% by weight of the compound (I) and may be applied at an application rate of from 3 to 10kg per 10 are.

The following detailed Examples, Formulations and Experiments are presented by way of illustration of the invention.

Example 1

2-Phenylimino-1,3-thiazolidin-3-thiolphosphonic acid O-methyl-S-sec-butyl ester (Compound No. 2)

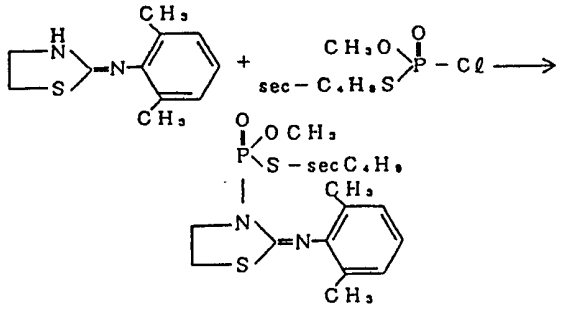


To the mixture of 2-phenylimino-1,3-thiazolidine (2.67g, 15.0mM), triethylamine (1.67g, 16.5mM) and benzene (30ml) is dropwise added monochlorothiolphosphoric acid O-methyl-S-sec-butyl ester (3.04g, 15.0mM) with stirring at temperature of 10 to 20°C. The mixture is allowed to react at 25 to 30°C for 3 hours. The resulting triethylamine hydrochloride is filtered off and the benzene layer is successively washed with 3% hydrochloric acid, 3% sodium bicarbonate and water, and concentrated under reduced pressure to give an oil. Yield: 5.12g.

The oil is purified by column chromatography over silica gel (Wako gel C-300) using n-hexane and acetone (=5:1). Fractions containing the ultimate product are combined and evaporated under reduced pressure to leave transparent colourless liquid. Yield: 3.58g (69.3%), $n_D^{25}=1.5833$

Example 2

2-(2,6-Dimethylphenyl)imino-1,3-thiazolidin-3-thiolphosphonic acid O-methyl-S-sec-butyl ester (Compound No. 4)



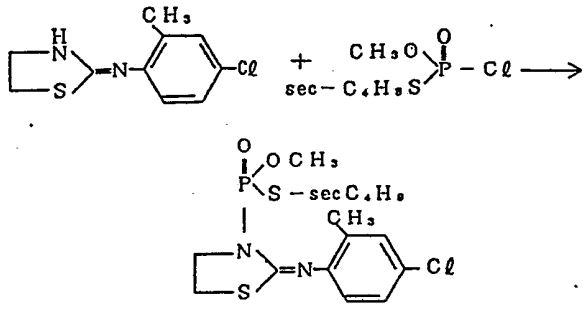
To the mixture of 2-(2,6-dimethylphenyl)imino-1,3-thiazolidine (2.06g, 10.0mM), triethylamine (1.11g, 11.0mM) and benzene (30ml) is dropwise added monochlorothiolphosphoric acid O-methyl-S-sec-butyl ester (2.03g, 10.0mM) with stirring at 10 to 20°C. The mixture is allowed to react at 25 to 30°C for 3 hours and the resulting triethylamine is filtered off. The benzene layer is successively washed with 3% hydrochloric acid, 3% sodium bicarbonate and water, and evaporated under reduced pressure to obtain an oil. Yield: 3.67g.

The oil is purified by column chromatography over silica gel (Wako gel C-300) using n-hexane and acetone (=10:1). The resulting transparent colourless viscous liquid is allowed to cool to yield a white crystal having a melting point of 61.5 to 63.5°C.

Example 3

2-(2-Methyl-4-chlorophenyl)imino-1,3-thiazolidin-3-thiolphosphonic acid O-methyl-S-sec-butyl

ester (Compound No. 6)

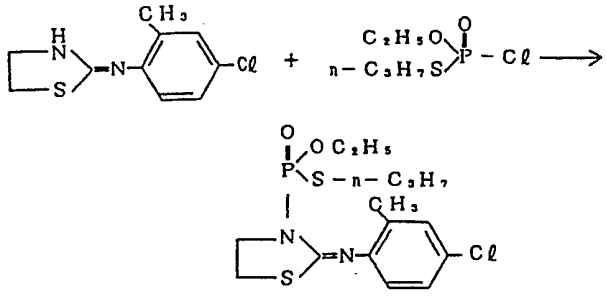


To the mixture of 2-(2-methyl-4-chlorophenyl)imino-1,3-thiazolidine (5.67g, 25.0mM), triethylamine (2.78g, 27.5mM) and toluene (50ml) is dropwise added monochlorothiolphosphoric acid O-methyl-S-sec-butyl ester (5.07g, 25.0mM) with stirring at 10 to 20°C. The mixture is allowed to react at 25 to 30°C, and the resulting triethylamine hydrochloride is filtered off. The toluene layer is successively washed with 3% hydrochloric acid, 3% sodium bicarbonate and water, and evaporated under reduced pressure to give an oil. Yield: 9.77g.

The oil is purified as described in Example 2 to give transparent colourless viscous liquid. Cooling of this liquid provides white crystal having a melting point of 60.5 to 62.5°C. Yield: 7.01g (71.2%).

Example 4

2-(2-Methyl-4-chlorophenyl)imino-1,3-thiazolidin-3-thiolphosphonic acid O-ethyl-S-n-propyl ester (Compound No. 7)

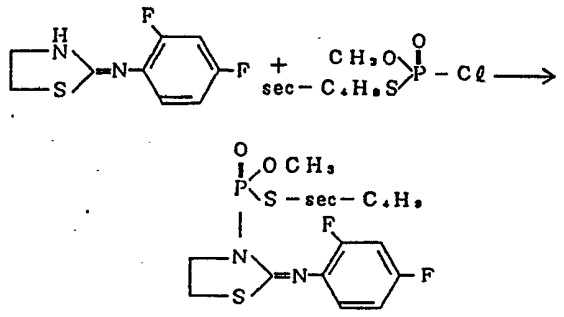


To the mixture of 2-(2-methyl-4-chlorophenyl)imino-1,3-thiazolidine (5.67g, 25.0mM), triethylamine (2.78g, 27.5mM) and toluene (50ml) is dropwise added monochlorothiolphosphoric acid O-ethyl-S-n-propyl ester (5.07g, 25.0mM) with stirring at 10 to 20°C. The mixture is allowed to react at 25 to 30°C for 3 hours, and the resulting triethylamine hydrochloride is filtered off. The toluene layer is successively washed with 3% hydrochloric acid, 3% sodium bicarbonate and water, and then evaporated under reduced pressure to give an oil. Yield: 9.64g.

The oil is purified as described in Example 2 to obtain transparent colourless liquid. Yield: 6.54g (66.4%), $n_D^{25} = 1.5817$.

Example 5

2-(2,4-Difluorophenyl)imino-1,3-thiazolidin-3-thiolphosphonic acid O-methyl-S-sec-butyl ester (Compound No. 11)

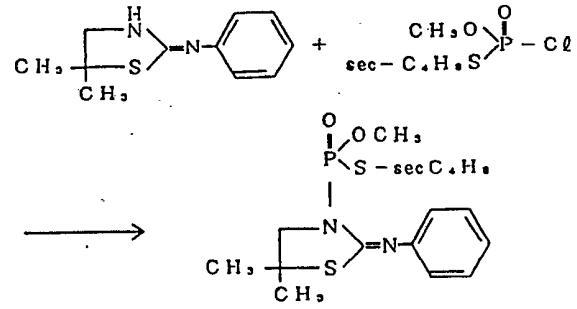


To the mixture of 2-(2,4-difluorophenyl)imino-1,3-thiazolidine (1.71g, 8.0mM), triethylamine (0.89g, 8.8mM) and benzene (30ml) is dropwise added monochlorothiolphosphoric acid O-methyl-S-sec-butyl ester (1.62g, 8.0mM) with stirring at 10 to 20°C. The mixture is allowed to react at 25 to 30°C for 5 hours, and the resulting triethyl amine hydrochloride is filtered off. The benzene layer is successively washed with 3% hydrochloric acid, 3% sodium bicarbonate and water, and then evaporated under reduced pressure to give an oil. Yield: 3.00g.

The oil is purified by column chromatography over silica gel (Wako gel C-300) using chloroform and ethyl acetate (=10:1) to provide transparent colourless viscous liquid. Yield: 1.95g (64.1%), $n_D^{25}=1.5526$.

Example 6

2-Phenylimino-5,5-dimethyl-1,3-thiazolidin-3-thiolphosphonic acid O-methyl-S-sec-butyl ester (Compound No. 17)



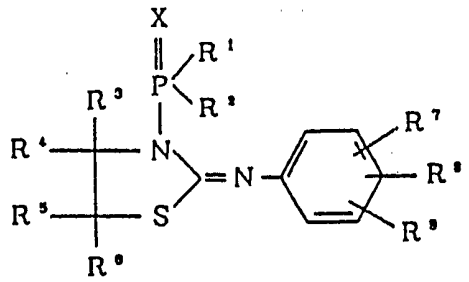
To the mixture of 2-phenylimino-5,5-dimethyl-1,3-thiazolidine (1.65g, 8.0mM), triethylamine (0.89g, 8.8mM) and benzene (30ml) is dropwise added monochlorothiolphosphoric acid (O-methyl-S-sec-butyl ester (1.62g, 8.0mM) with stirring at 10 to 20°C. The mixture is allowed to react at 25 to 30°C for 3 hours, and the resulting triethylamine hydrochloride is filtered off. The benzene layer is successively washed with 3% hydrochloric acid, 3% sodium bicarbonate and water, and then evaporated under reduced pressure to give an oil. Yield: 2.97g.

The oil is purified by column chromatography over silica gel (Wako gel C-300) using n-hexane and ethyl acetate (=6:1) to provide transparent colourless viscous liquid. Yield: 1.74g (58.4%), $n_D^{25}=1.5634$.

Example 7–20

In substantial accordance with the procedures as taught in Examples 1 to 6, a variety of compounds (I) of the present invention were prepared. Physico-chemical properties of the compounds are listed in Table 1. NMR and IR data for the compounds listed in Table 1 are summarized in Table 3. In addition, an elementary analysis was conducted for several compounds selected from the compounds listed in Table 1. The results are shown in Table 2.

Table 1



(I)

Compound No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	X	Appearance	Physico-chemical properties: m.p. (°C)	Physico-chemical properties: Refractive Index
1	EtO	n-Pr-S	H	H	H	H	H	H	H	O	transparent colourless liquid		n_D^{25} 1.5827
2	MeO	s-Bu-S	H	H	H	H	H	H	H	O	transparent colourless liquid		n_D^{25} 1.5833
3	EtO	i-Bu-S	H	H	H	H	H	H	H	O	transparent colourless liquid		n_D^{25} 1.5756
4	MeO	sec-Bu-S	H	H	H	H	2-Me	H	6-Me	O	white crystal	61.5-63.5	
5	EtO	n-Pr-S	H	H	H	H	2-Me	H	6-Me	O	white crystal	60.0-62.0	
6	MeO	s-Bu-S	H	H	H	H	2-Me	4-Cl	H	O	white crystal	60.5-62.5	
7	EtO	n-Pr-S	H	H	H	H	2-Me	4-Cl	H	O	transparent colourless liquid		n_D^{20} 1.5817

Table 1 (cont'd)

Compound No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	X	Appearance	Physico-chemical properties: m.p. (°C)	Physico-chemical properties: Refractive Index
8	EtO	EtO	H	H	H	H	2-Me	4-Cl	H	S	transparent colourless liquid		n_D^{25} 1.5839
9	EtO	n-Pr-S	H	H	H	H	2-Me	4-Cl	H	S	transparent colourless liquid		n_D^{25} 1.6078
10	EtO	n-Pr-S	Me	Me	H	H	H	H	H	O	transparent colourless liquid		n_D^{25} 1.5435
11	MeO	s-Bu-S	H	H	H	H	2-F	4-F	H	O	transparent colourless viscous liquid		n_D^{25} 1.5526
12	EtO	n-Pr-S	H	H	H	H	2-F	4-F	H	O	transparent colourless viscous liquid		n_D^{25} 1.5587
13	MeO	s-Bu-S	H	H	Me	Me	H	4-Cl	H	O	transparent colourless viscous liquid		n_D^{25} 1.5691
14	EtO	n-Pr-S	H	H	Me	Me	H	4-Cl	H	O	transparent colourless viscous liquid		n_D^{25} 1.5698
15	MeO	s-Bu-S	H	H	Me	Me	2-Me	4-Cl	H	O	transparent colourless viscous liquid		n_D^{25} 1.5645
16	EtO	n-Pr-S	H	H	Me	Me	2-Me	4-Cl	H	O	transparent colourless viscous liquid		n_D^{25} 1.5608
17	MeO	s-Bu-S	H	H	Me	Me	H	H	H	O	transparent colourless viscous liquid		n_D^{25} 1.5634
18	EtO	n-Pr-S	H	H	Me	Me	H	H	H	O	transparent colourless viscous liquid		n_D^{25} 1.5637
19	MeO	s-Bu-S	Me	Me	H	H	H	H	H	O	transparent yellow liquid		n_D^{25} 1.5625
20	EtO	n-Pr-S	Me	Me	H	H	2-Et	H	6-Et	O	white crystal	102.0-104.0	

Table 2

Compound No.		C	H	N	P
1	Calculated: ($C_{14}H_{21}N_2O_2PS_2$)	48.82	6.15	8.13	
	Found:	48.32	6.03	7.92	
2	Calculated: ($C_{14}H_{21}N_2O_2PS_2$)	48.82	6.15	8.13	
	Found:	48.46	6.06	8.05	
7	Calculated: ($C_{15}H_{22}N_2O_2PS_2Cl$)	45.85	5.64	7.13	
	Found:	45.45	5.61	7.06	
6	Calculated: ($C_{15}H_{22}N_2O_2PS_2Cl$)	45.85	5.64	7.13	7.88
	Found:	45.48	5.55	6.86	7.14
5	Calculated: ($C_{16}H_{25}N_2O_2PS_2$)	51.59	6.76	7.52	
	Found:	51.95	6.95	7.39	
4	Calculated: ($C_{16}H_{25}N_2O_2PS_2$)	51.59	6.76	7.52	
	Found:	51.02	6.62	7.10	

Table 3

Compound No.	NMR* (ppm)	IR** (cm^{-1})
1	1.00(3H,t,J=7.0Hz,CH_3 of -S-nPr), 1.37(3H,t,J=7.0Hz, CH_3 of OEt), 1.66(2H,m,S$\frown$$CH_2$$\frown$), 2.7-3.3(2H,m,$SCH_2$$\frown$), 3.20(2H,t,J=6.0Hz,thiazolidine C_5-H), 3.9-4.5(4H,m, Ch_2 of OEt,thiazolidine C_4-H), 6.8-7.5(5H,m,aromatic H)	1240(broad, -P(=O)$\diagup\diagdown$) 1640(C=N-)
2	1.00(3H,t,J=7.0Hz,CH_3 of S-secBu), 1.45(3H,dd,J=7.0, 1.0Hz,CH_3 of S-secBu), 3.20(2H,t,J=6.5Hz,thiazolidine C_5-H), 3.4-4.2(3H,m,CH of S-secBu,thiazolidine C_4-H), 3.87(3H,d,J=13.0Hz,OCH_3), 6.8-7.5(5H,m,aromatic H)	1240(broad, -P(=O)$\diagup\diagdown$) 1640(C=N-)
3	1.00(6H,d,J=6.0Hz,CH_3x2 of S-isoBu), 1.38(3H,t,J=7.0Hz, CH_3 of OEt), 1.5-2.0(1H,m,CH of S-isoBu), 2.5-3.3(2H,m, CH_2 of S-isoBu), 3.40(2H,t,J=7.0Hz,thiazolidine C_5-H), 3.9-4.5(4H,m,CH_2 of OEt,thiazolidine C_4-H), 6.8-7.3(5H, m,aromatic H)	1230(broad, -P(=O)$\diagup\diagdown$) 1640(C=N-)
7	1.03(3H,t,J=7.0Hz,CH_3 of S-n-Pr), 1.38(3H,t,J=7.0Hz, CH_2 of OEt), 1.70(2H,m,S$\frown$$CH_2$$\frown$), 2.20(3H,s,$\phi$-$CH_3$), 2.7-3.5(2H,m,$SCH_2$$\frown$), 3.23(2H,t,J=6.0Hz,thiazolidine C_5-H), 3.9-4.5(4H,m,CH_2 of OEt,thiazolidine C_4-H), 6.6-7.2(3H,m,aromatic H)	1230(broad, -P(=O)$\diagup\diagdown$) 1640(C=N-)
8	1.35(6H,t,J=7.0Hz,CH_3 of OEt), 2.17(3H,s,ϕ-CH_3), 3.16 (2H,t,J=7.0Hz,thiazolidine C_5-H), 4.0-4.5(6H,m,CH_2 of OEt,thiazolidine C_4-H), 6.6-7.2(3H,m,aromatic H)	1635(C=N-)
20	1.03(3H,t,J=7.0Hz,CH_3 of S-nPr), 1.13 and 1.20(3Hx2,t, J=7.0Hz,CH_3x2 of ϕ-Et),1.38(3H,t,J=7.0Hz,CH_3 of OEt), 1.67(2H,m,S$\frown$$CH_2$$\frown$), 1.75(6H,d,J=4.0Hz,gem-diCH_3 of thiazolidine), 2.50(4H,q,J=7.0Hz,CH_2x2 of ϕ-Et), 2.7-3.2(4H,m,$SCH_2$$\frown$,thiazolidine C_5-H), 4.0-4.5(2H,m,CH_2 of OEt), 7.05(3H,s,aromatic H)	1240(broad, -P(=O)$\diagup\diagdown$) 1620(C=N-)

Table 3(cont'd)

6	1.00(3H,t,J=7.0Hz,CH_3 of S-secBu), 1.43(3H,dd,J=7.0, 1.0Hz, CH_3 of S-secBu), 1.70(2H,m,CH_2 of S-secBu), 2.17 (3H,s,ϕ-CH_3), 3.20(2H,t,J=7.0Hz,thiazolidine C_5-H), 3.4-4.3(3H,m,CH_2 of OEt,thiazolidine C_5-H), 3.85(3H,d, J=14.0Hz,OCH_3), 6.6-7.2(3H,m,aromatic H)	1230(broad, -P=O) 1640(C=N-)
11	1.00(3H,t,J=7.0Hz,CH_2 of S-secBu), 1.45(3H,dd,J=7.0, 1.0Hz,CH_3 of S-secBu), 1.70(2H,m,CH_2 of S-secBu), 3.27 (2H,t,J=7.0Hz,thiazolidine C_5-H), 3.4-4.3(3H,m,CH of S-secBu,thiazolidine C_4-H), 3.90(3H,d,J=13.0Hz,OCH_3), 6.7-7.2(3H,m,aromatic H)	1240(broad, -P(=O)<) 1635(C=N-)
12	1.00(3H,t,J=7.0Hz,CH_3 of S-nPr), 1.40(3H,t,J=7.0Hz,CH_3 of OEt), 1.65(2H,m,SCH_2), 2.7-3.5(2H,m,SCH_2), 3.27(2H,t,J=7.0Hz,thiazolidine C_5-H), 3.9-4.4(4H,m,CH_2 of OEt,thiazolidine C_4-H),6.6-7.0(3H,m,aromatic H)	1240(broad, -P(=O)<) 1630(C=N-)
4	1.03(3H,t,J=7.0Hz,CH_3 of S-secBu), 1.45(3H,d,J=7.0Hz, CH_3 of S-secBu), 1.70(2H,m,CH_2 of S-secBu), 2.16 and 2.20(3Hx2,brSϕ-CH_3x2), 3.20(2H,t,J=7.0Hz,thiazolidine C_5-H), 3.4-4.3(3H,m,CH of S-secBu,thiazolidine C_4-H), 3.90(3H,d,J=14.0Hz,OCH_3), 6.98(3H,s,aromatic H)	1240(broad, -P(=O)<) 1640(C=N-)
5	1.03(3H,t,J=7.0Hz,CH_3 of S-nPr), 1.40(3H,t,J=7.0Hz,CH_3 of OEt), 1.70(2H,m,SCH_2), 2.15 and 2.20(3Hx2,brSϕ-CH_3x2),2.8-3.3(2H,m,SCH_2), 3.20(2H,t,J=7.0Hz,thiazolidine C_5-H), 3.9-4.5(4H,m,CH_2 of OEt,thiazolidine C_4-H), 7.00(3H,s,aromatic H)	1240(broad, -P(=O)<) 1640(C=N-)
13	1.03(3H,t,J=7.0Hz,CH_3 of S-secBu), 1.43(3H,dd,J=7.0, 1.0Hz,CH_3 of S-secBu), 1.53(6H,s,thiazolidine gem-diCH_3), 1.70(2H,m,CH_2 of S-secBu), 3.43(2H,d,J=2.0Hz,thiazolidine C_4-H),3.90(3H,d,J=13.0Hz,OCH_3), 7.05(4H,dd,J=24.0, 9.0Hz, aromaticH)	1240(broad, -P(=O)<) 1640(C=N-)

Table 3 (cont'd)

14	1.00(3H,d,J=7.0Hz,CH_3 of S-nPr), 1.40(3H,t,J=7.0Hz,CH_3 of OEt),1.53(6H,s,thiazolidine gem-diCH_3), 1.70(2H,m, S$\frown$$CH_2$), 3.03(2H,dt,J=15.0,7.0Hz,SCH_2), 3.85(2H,d, J=2.0Hz,thiazolidine C_4-H), 4.30(2H,m,CH_2 of OEt), 7.06 (4H,dd,J=24.0, 9.0Hz,aromatic H)	1240(broad, -P=O), 1630(C=N-)
15	1.03(3H,t,J=7.0Hz,CH_3 of S-secBu), 1.45(3H,dd,J=7.0, 1.0Hz,CH_3 of S-secBu), 1.53(6H,s,thiazolidine gem-diCH_3), 1.70(2H,m,CH_2 of S-secBu), 2.20(3H,s,ϕ-CH_3), 3.4-3.7(1H, m,CH of S-secBu), 3.85(2H,d,J=2.0Hz,thiazolidine C_4-H), 3.86(3H,d,J=13.0Hz,OCH_3), 6.6-7.2(3H,m,aromatic H)	1240(broad, -P=O), 1630(C=N-)
16	1.00(3H,t,J-7.0Hz,CH_3 of S-nPr), 1.40(3H,t,J=7.0Hz,CH_3 of OEt), 1.53(6H,s,thiazolidine gem-diCH_3), 1.70(2H,m, S$\frown$$CH_2$), 2.20(3H,s,$\phi$-$CH_3$), 3.03(2H,dt,J=15.0,7.0Hz, S-CH_2), 3.87(2H,d,J=2.0Hz,thiazolidine C_4-H), 4.30(2H, m,CH_2 of OEt), 6.6-7.2(3H,m,aromatic H)	1240(broad, -P=O), 1630(C=N-)
17	1.00(3H,t,J=7.0Hz,CH_3 of S-secBu), 1.43(3H,dd,J=7.0, 1.0Hz,CH_3 of S=secBu), 1.53(6H,s,thiazolidine gem-diCH_3), 1.73(2H,m,CH_2 of S-secBu), 3.4-3.9(1H,m,CH of S-secBu), 3.83(2H,d,J=2.0Hz,thiazolidine C_4-H), 3.88(3H,d,J=13.0Hz, OCH_3), 6.8-7.3(5H,m,aromatic H)	1240(broad, -P=O), 1630(C=N-)
18	1.00(3H,t,J=7.0Hz,CH_3 of S-nPr), 1.36(3H,t,J=7.0Hz,CH_3 of OEt), 1.50(6H,s,thiazolidine gem-diCH_3), 1.70(2H,m,S$\frown$$CH_2$), 3.00(2H,dt,J=15.0,9.0Hz,SCH_2), 3.80(2H,d,J=2.0Hz, thiazolidine C_4-H), 4.30(2H,m,CH_2 of OEt), 6.8-7.3(5H,m, aromatic H)	1240(broad, -P=O), 1630(C=N-)

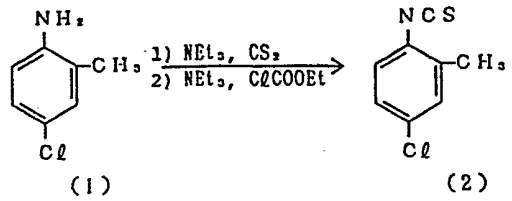
* Solvent: $CHCl_3$, Internal Standard: T.M.S.

** Solvent: $CHCl_3$

The process for preparing the starting compounds employed in the present invention are exemplified below.

Preparation 1

2-(2-Methyl-4-chlorophenyl)imino-1,3-thiazolidine (*3*)

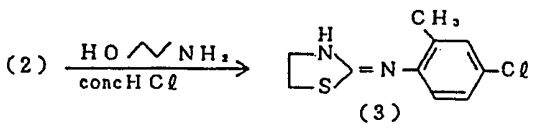


(1) (2)

1. 2-Methyl-4-chlorophenyl isothiacyanate (*2*)

4-Chloro-2-methylaniline (*1*) (26.1g) is dissolved in benzene (40ml). To the solution is added triethylamine (18.6g). After ice-cooling, carbon disulfide (14.0g) is dropwise added with stirring over 15 minutes. The reaction mixture is then allowed to warm to room temperature and stirred for 45 minutes. The mixture is allowed to stand overnight in a refrigerator and evaporated to remove the benzene. The residue is dissolved in chloroform (100ml), and triethylamine (18.6g) is added to the resulting solution. After addition of ethyl chloroformate (20.0g) over 10 minutes with stirring and ice-cooling, the reaction mixture is allowed to warm to room temperature, stirred for 3 hours, added with conc. HCl (40ml) dissolved in water (250ml), and extracted with chloroform. The chloroform extract is washed with water, dried over Na_2SO_4, and evaporated to remove the solvent. The aimed semi-crystal product (*2*) is thus obtained as the residue. Yield: 30.3g (90%). Melting point after purified by silica gel chromatography is 31.5–32.5°C.

2. 2-(2-Methyl-4-chlorophenyl)imino-1,3-thiazolidine (*3*)

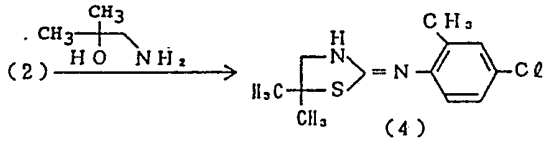


(3)

The compound (*2*) obtained above (12.93g) is charged in an eggplant type flask (200ml volume) and 2-aminoethanol (4.32g) is added thereto. After thorough agitation and heating, the mixture is cooled and conc. HCl (25ml) is added. The mixture is heated under reflux for 2 hours, cooled, and made basic by addition of 4N NaOH. The precipitated crystal is filtered, washed with water, dried, and recrystallized from methanol. Colourless columnar crystal of the aimed product (*3*) is thus obtained. m.p.: 137–139°C. Yield: 9.0g (57%).

Preparation 2

2-(2-Methyl-4-chlorophenyl)imino-5,5-dimethyl-1,3-thiazolidine (*4*)



(4)

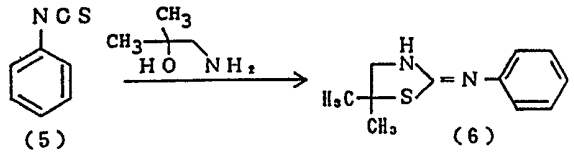
The compound (*2*) obtained above (5.0g) is placed in an eggplant type flask (100ml volume) and (1-amino-2-methyl)-2-propanol (2.43g) is added thereto. After addition of chloroform (20ml), the mixture is stirred, evaporated to remove the chloroform, added with conc. HCl (10ml), refluxed for 40 minutes, cooled, made basic with 4N NaOH, and extracted with chloroform. The chloroform extract is washed with water, dried over Na_2SO_4, evaporated to remove the chloroform, added with benzene, and filtered to remove insoluble substances. Addition of n-hexane to the filtrate yields the aimed product (*4*) as a colourless needle. m.p.: 127.5–130.0°C, Yield: 2.30g (33%).

Elementary Analysis ($C_{12}H_{15}N_2SCl$)

	C	*H*	*N*
Calculated (%):	56.57	5.93	10.99
Found (%):	56.50	5.84	10.90

Preparation 3

2-Phenylimino-5,5-dimethyl-1,3-thiazolidine (6)



(5) (6)

Phenyl isothiacyanate (*5*) (1.97g) is placed in an eggplant type flask (50ml volume) and (1-amino-2-methyl)-2-propanol (1.30g) is added thereto. The mixture is throughly agitated and heated. After cooling, conc.HCl (15ml) is added and the mixture is heated under reflux for 3 hours, cooled, and made basic with 4N NaOH. The reaction mixture is extracted with chloroform, and the chloroform extract is washed with water, dried over Na_2SO_4, evaporated to remove the chloroform, and purified by silica gel chromatography. After recrystallization from methanol, the aimed product (*6*) having a melting point of 153–155.0°C is obtained. Further recrystallization of the product from benzene/n-hexane gives colourless flake having a melting point of 148–151°C. Yield: 1.7g (56%).

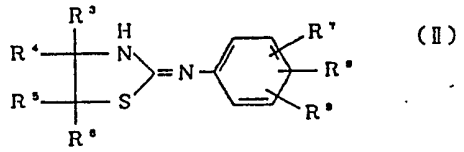
Elementary Analysis ($C_{11}H_{14}N_2S$)

	C	*H*	*N*
Calculated (%):	64.04	6.48	13.58
Found (%):	63.81	6.79	13.44

Preparations 4–9

The following starting compounds (II) listed in Table 4 are obtained in the similar manner as described in the foregoing preparations.

Table 4



(II)

Preparation No.	R^3	R^4	R^5	R^6	R^7	R^8	R^9	m.p. (°C)	yield (%)
1	H	H	H	H	2-Me	4-Cl	H	137–139	57
2	H	H	Me	Me	2-Me	4-Cl	H	127.5–130.0	33
3	H	H	Me	Me	H	H	H	148–151	56
4	H	H	H	H	H	H	H	159–162	85
5	H	H	H	H	2-F	4-F	H	148–149	56
6	H	H	H	H	2-Me	H	6-Me	92–93	53
7	Me	Me	H	H	H	H	H	158–160	48
8	Me	Me	H	H	2-Et	H	6-Et	142–144	62
9	H	H	Me	Me	H	4-Cl	H	143.0–146.5	30

Pesticidal compositions containing as an active ingredient a compound of the invention are illustrated below.

Formulation 1 Dust

Ingredient	*Part by weight*
Compound No. 1	2
Clay	88
Talc	10

The above ingredients are admixed to obtain a dust preparation.

Formulation 2 Wettable powder

Ingredient	*Part by weight*
Compound No. 3	30
Diatomaceous earth	45
White carbon	20
Sodium lauryl sulfate	3
Sodium lignin sulfonate	2

The above ingredients are admixed to obtain a wettable powder preparation.

Formulation 3

Ingredient	*Part by weight*
Compound No. 5	20
Xylene	60
Polyoxyethylenephenyl-phenolpolymer	20

The above ingredients are admixed to obtain an emulsifiable concentrate preparation.

Pesticidal activity of the compounds of the invention was determined in accordance with the following procedures.

Test 1

Samples

The compound (I) of the invention to be tested is dissolved in a minimum amount of DMF. Distilled water containing Tween 20 at the concentration of 100ppm is thereto added to prepare a series of samples of the desired concentrations.

Test Procedure

A. Suppression of *Spodoptera litura* larvae

Cabbage leaves (7×7cm) were immersed in the sample solution as prepared above and air dried. Two leaves were placed in a petri dish (9cm diameter) and 10 second-instar larvae of *Spodoptera litura* were placed in the dish. The dish was held at 25°C and the mortality of the larvae was determined after 48 hours.

C. Suppression of *Plutella xylostella* larvae

Cabbage leaf (7×7cm) was immersed in the sample solution and air dried. The leaf was placed in a petri dish (9cm diameter) and 10 third-instar larvae of *Plutella xylostella* were placed in the dish. The dish was held at 25°C and the mortality of the larvae was determined after 48 hours.

D. Suppression of *Adoxophyes sp.* larvae

Whole tea leaves were immersed in the sample solution and air dried. Three leaves were placed in a polyethylene petri dish (6cm diameter, 4cm depth) and 10 forth-instar larvae of *Adoxophyes sp.* were placed in the dish. The dish was held at 25°C and the mortality of the larvae was determined after 48 hours.

E. Suppression of *Nephotettix cincticeps* larvae (sensitive strain)

Six or seven rice seedlings of 1.5 to 2 plant age in leaf number were bundled and the foliar parts of the seedlings were sprayed with 2ml of the sample solution and air dried. The treated seedlings were covered with a transparent plastic cylinder and ten female larvae were placed in the cylinder. The atmosphere in the cylinder was kept at 25°C, and the mortality after 48 hours was determined.

I. Suppression of *Myzus persicae* larvae (sensitive strain)

A polyethylene cup (diameter 6cm, depth 4cm) was filled with 0.3% agar gel and a piece of Chinese cabbage leaf (3×3cm) was placed on the gel. After infesting with second instar larvae on the piece of leaf, 2ml of the sample solution was sprayed on the cup. The test system was kept at 25°C for 48 hours and the mortality of the larvae was determined.

J. Suppression of *Myzus persicae* larvae (Resistant)

The same test procedure as above was repeated on *Myzus persicae* resistant.

M. Suppression of *Tetranychus cinnabrinus*

A polyethylene cup (diameter 6cm, depth 4cm) was filled with 0.3% agar gel and a piece of

kidney bean leaf (diameter 2cm) was placed on the gel. Twelve adults of *Tetranychus cinnabrinus* were placed on the leaf. After 24 hours at 25°C, dead and feeble worms were removed and 2ml of the sample solution was sprayed on the cup. Following such treatment the test system was kept at 25°C and the mortality was determined after 48 hours.

O. Suppression of *Tetranychus urticae*

The same test procedure as above was repeated on *Tetranychus urticae.*

N. Suppresion of *Tetranychus cinnabrius* eggs

A polyethylene cup (diameter 6cm, depth 4cm) was filled with 0.3% agar gel and a piece of bush bean leaf (diameter 2cm) was placed on the gel. Seven female adults of *Tetranychus cinnabrius* were placed on the leaf and allowed to egg-deposit while keeping the surrounding atmosphere at 25°C over 24 hours. After removing the adults, 2ml of the sample was sprayed on the leaf under a rotary application tower. The test system was kept at 25°C for 7 days and the mortality of eggs was determined by counting the number of eggs which did not hatch.

P. Suppression of *Tetranychus urticae* eggs

The same test procedure as above was repeated on *Tetranychus urticae* eggs.

T. Suppression of *Henosepilachna vigintioctopunctata* (twenty-eight-spotted beetle) adults

Japanese eggplant leaf (6×6cm) was immersed in the sample solution and air dried. The leaf was placed in a petri dish (9cm diameter) and 5 adults of *Henosepilachna vigintioctopunctata* were placed in the dish. The dish was held at 25°C and the mortality was determined after 48 hours.

S. Suppression of *Popillia japonica* (Japanese beetle) adults

The same test procedure as above was repeated on *Popillia japonica* adults.

R. Suppression of *Periplaneta americana* larvae

A filter paper soaked with the sample solution was placed in a petri dish (diameter 9cm). Five *Periplaneta americana* larvae within 7 days after hatching were placed in the dish hold at 25°C and the mortality after 48 hours was measured.

Table 5 shows the test results in terms of mortality (%) of the worms wherein the following codes are employed.

A:	*Spodoptera litura*	(larvae)
C:	*Plutella xylostella*	(larvae)
D:	*Adoxophyes* sp.I	(larvae)
E.	*Nephotettix cincticeps*	(larvae)
I:	*Myzus persicae* sensitive	(larvae)
J:	*Myzus persicae* Resistant	(larvae)
M:	*Tetranychus cinnabrinus*	(adult)
O:	*Tetranychus urticae*	(adult)
N:	*Tetranychus cinnabrinus*	(egg)
P:	*Tetranychus urticae*	(egg)
R:	*Periplaneta americana*	(larvae)
S:	*Popillia japonica*	(adult)
T:	*Henosepilachna vigintioctopunctata*	(adult)

Table 5

Compound No.	conc. (ppm)	A	C	D	E	I	J	M	N	O	P	R	S	T
1	1000	65				58		100	-			100		100
	250							100		95			100	0
	63							100		35		100	95	0
	16							55		1		10	0	0
	4							9				0		
2	1000	-			-	-		100	-			100		100
	250							100		100			100	40
	63							100		89		90	94	0
	16							100		6		20	5	0
	4							57				0		
3	1000	60			-	83		100	-			100		100
	250							100		73			37	100
	63							100		67		100	58	20
	16							95		11		0	42	0
	4							20				0		
7	1000	100			7	95		100	92			100		100
	250	100	70	100				100	94	100	27			80
	63	100	70	90				100	83	100	25	90		60
	16	45	40	20				100	27	77	2	30		0
	4							100				0		
8	1000	0			17	28		0	79			100		0
	63											0		
	16											0		
	4											0		

Table 5 (cont'd)

Compound No.	conc. (ppm)	A	C	D	E	I	J	M	N	O	P	R	S	T
9	1000	100			8	0		0	11			100		80
	250	0	45	10										
	63	0	35	0								0		
	16	0	5	0								0		
	4											0		
19	250	0			0	90	6	100	0	89		0		0
	63					10	0	94		8				
	16					5	0	7		0				
	4													
20	1000	100			0	0		100	0			100		100
	250	95	65	0				100		46				100
	63	15	15	10				100		23		20		90
	16	0	10	0				83		0		0		20
	4							7				0		
6	1000	100			73	100		100	77			100		100
	250	100	100	100	50	100	19	100	87	100	27			100
	63	100	100	100	6	95	7	100	66	100	17	90		40
	16	55	70	40	7	18	0	100	38	80	0	0		0
	4							100				0		
11	250	40	50	80		100	64	100	78	100	54			100
	63	5	25	10		11	0	100	74	100	13			30
	16	0	0	5		0	6	100	0	28	0			0
	4							51						

Table 5 (cont'd)

Compound No.	conc. (ppm)	A	C	D	E	I	J	M	N	O	P	R	S	T
12	1000	100		100		69		100	100	100	100			100
	250	95	10	90				100	99	100	97			100
	63	10	0	35				100	93	100	47			90
	16	0		5				100	21	21	1			10
	4							100						
4	1000	100			89	100		100	100			100		100
	250	85	70	100		100	29					60		100
	63	35	20	0		80	0					0		80
	16	0	5	0		3	0					0		20
5	1000	-			-	74		100	22			-		-
13	1000	100			100	100		100				100		
	250	100	100	100	5	100	47	100	100	100	0			100
	63	40	90	75	0	50	0	100	95	100	3			100
	16	0	70	10	8	0	0	100	30	69	0			50
	4							100						
14	1000	100			100	100		100				100		
	250	100	60	100	5	58	0	100	100	100	28			100
	63	15	20	85	0	0	0	100	100	100	12			100
	16	0	0	20	5	0	8	100	70	84	0			83
	4							77						
15	1000	100			100	100		100				100		
	250	100	100	100	4	100	4	100	100	100	11			100
	63	70	20	75	0	41	0	100	85	100	4			100
	16	0	20	20	0	0	0	100	7	86	3			33
	4							100						

Table 5 (cont'd)

Compound No.	conc. (ppm)	A	C	D	E	I	J	M	N	O	P	R	S	T
16	1000	100			100	100		100				100		
	250	100	70	85	0	20	0	100	100	100	10			100
	63	75	50	15	0	0	0	100	69	100	3			100
	16	15	20	5	0	0	0	100	0	93	0			67
	4							91						
17	1000	100			100	100	69	100				100		
	250	95	100	95	0	100	17	100	83	100	1			100
	63	20	100	0	9	43	0	100	22	100	5			17
	16	5	30	0	0	0		100	0	36	0			0
	4							100	0					
18	1000	100			100	100		100				100		
	250	75	40	35	0	36	0	100	95	100	9			83
	63	5	30	5	0	0	0	100	45	97	1			33
	16	0	0	0	8	0	0	100	0	19	0			0
	4							44						

Test 2

The acaricidal activity of the compounds (I) was determined using *Pentamerismus oregonensis* which had been collected in the open air and subcultured on a rabbit (40 days-old after molting).

A piece of filter paper was placed on a petri dish (9cm diameter), and 20 *Pentamerismus oregonenis* were left thereon. Two milliliter of the sample solution adjusted so as to contain 0.1% by weight of Compound No. 6 was sprayed over the mites. The similar procedure was repeated using distilled water, which served as a control.

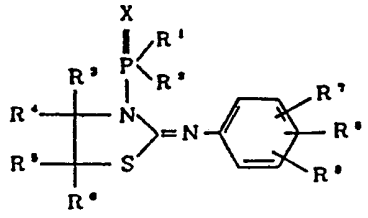
After 24 and 48 hours, mortality of the mites was determined and compared with that of the control. The death of the mites was recognized by no action against CO_2 gas and physical stimulation. The test results are shown in Table 6.

Table 6

Concentration (pp)m	Number of mites	*Number of dead mites* 24hrs.	48hrs.	Mortality (%)
1,000	20	20	—	100
500	20	19	1	100
250	20	18	2	100
125	20	19	0	95
control	20	0	0	0

CLAIMS

1. A compound of the formula



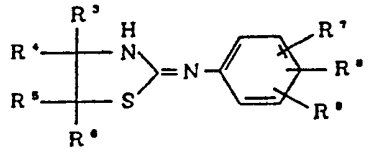
(I)

wherein R^1 and R^2 each independently represent C_1–C_5 alkoxy or C_1–C_5 alkylthio, R^3, R^4, R^5 and R^6 each independently represent hydrogen or C_1–C_5 alkyl, R^7, R^8 and R^9 each independently represent hydrogen, C_1–C^5 alkyl or halogen, and X represents oxygen or sulfur.

2. A compound as claimed in claim 1 wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8 and/or R^9 are/is selected from examples thereof given hereinbefore.

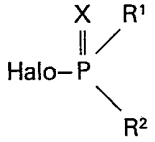
3. A compound as claimed in claim 1 and referred to hereinbefore.

4. A process for preparing a compound as defined in claim 1 which comprises reacting a compound of the formula:



(II)

with a compound of the formula:



wherein Halo is a leaving group, e.g. halogen.

5. A process as claimed in claim 4, wherein the starting compound of formula (II) has been prepared in a manner substantially as hereinbefore

6. A process as claimed in claim 5, wherein the starting compound of formula (II) has been prepared in a manner substantially as hereinbefore described in any one of Preparations 1 to 9.

7. A process as claimed in claim 4 and substantially as hereinbefore described in anyone of the Examples.

8. A pesticidal formulation which comprises a compound as defined in claim 1 formulated for pesticidal use and optionally together with a suitable carrier or adjuvant.

9. A formulation as claimed in claim 8 and substantially as hereinbefore described.

10. A formulation as claimed in claim 8 and substantially as hereinbefore described in any one of Formulations 1 to 3.

11. A method of killing or inhibiting the growth of pests which comprises applying to the environment thereof a compound as claimed in any one of claims 1 to 3 or a formulation as claimed in any one of claims 8 to 10.

12. A method as claimed in claim 11 and substantially as hereinbefore described.

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