

1

3,719,686

THIOPHOSPHATE DERIVATIVES OF TRIAZOLINE THIONES

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U.S. Cl. 260—308 C

11 Claims

ABSTRACT OF THE DISCLOSURE

A novel composition of matter comprising phosphate derivatives of Δ^2 -1,2,4-triazoline compounds having highly desirable utility as insecticides and acaricides.

BACKGROUND OF THE INVENTION

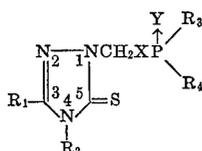
This application is a continuation-in-part application of Ser. No. 835,221, filed June 20, 1969, now abandoned.

The present invention relates to the synthesis of novel compositions comprising phosphate derivatives of certain 3-substituted- Δ^2 -1,2,4-triazoline compounds. More particularly, it relates to phosphate derivatives of 3-fluoroalkyl- Δ^2 -1,2,4-triazoline-5-thiones and 3-chlorodifluoromethyl- Δ^2 -1,2,4-triazoline-5-thiones compounds which have desirable use as insecticides and acaricides. Furthermore, it relates to methods for using such compounds in various agricultural applications.

A somewhat related compound is shown in the art, for example, 1-diethoxyphosphinothioylthiomethyl-3,4-dimethyl- Δ^2 -1,2,4-triazoline-5-thione [J. Sci. Fd. Agric., 19, 475-80 (1968)]. Such compound is reported to have both insecticidal and acaricidal activity. The compound is only generally related to those compounds of the present invention.

SUMMARY OF THE INVENTION

The present invention relates to phosphate derivatives of Δ^2 -1,2,4-triazoline-5-thione compounds and may be broadly represented as having the structure:



(I)

wherein

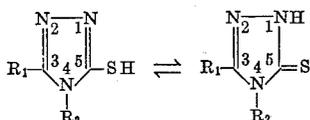
R_1 represents fluoroalkyl radicals having from 1 to 7 carbon atoms or a chlorodifluoromethyl radical,
 R_2 represents lower alkyl radicals having from 1 to 7 carbon atoms,

R_3 and R_4 independently represent alkyl, alkoxy or alkyl-amino radicals having from 1 to 7 carbon atoms or phenyl radicals, and

X and Y are independently oxygen or sulfur.

The particular compounds having the Structure (I) have shown a high degree of activity as broad spectrum insecticides and acaricides.

Included within the scope of the present invention are intermediate triazoline compounds which may be employed in preparing the compounds of Structure (I). Such compounds are capable of existing in tautomeric form and have the general structure:



(II)

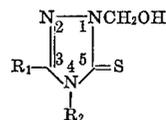
2

wherein

R_1 represents fluoroalkyl radicals having from 1 to 7 carbon atoms or a chlorodifluoromethyl radical, and

R_2 represents lower alkyl radicals having from 1 to 7 carbon atoms.

Also included in the scope of the present invention are other intermediate triazoline compounds having the general structure:

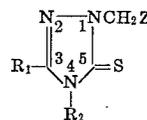


(III)

wherein

R_1 represents fluoroalkyl radicals having from 1 to 7 carbon atoms or a chlorodifluoromethyl radical, and
 R_2 represents lower alkyl radicals having from 1 to 7 carbon atoms.

Furthermore, included within the scope of the present invention are still other intermediate triazoline compounds having the general structure:



(IV)

wherein

R_1 represents fluoroalkyl radicals having from 1 to 7 carbon atoms or a chlorodifluoromethyl radical

R_2 represents lower alkyl radicals having from 1 to 7 carbon atoms, and

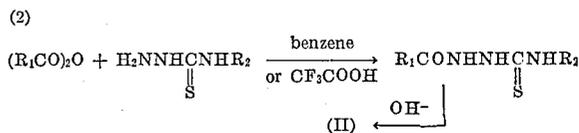
Z represents a halogen such as chlorine, bromine or iodine.

The symbols R_1 , R_2 , R_3 and R_4 have the same representations throughout the specification and claims.

Although the compounds represented by the Structures (II), (III), and (IV) have not demonstrated any particular insecticidal or acaricidal properties, they have utility in the preparation of the compounds represented by Structure (I) which has shown a high degree of activity as a broad spectrum insecticide and acaricide.

PREFERRED EMBODIMENTS OF THE INVENTION

The preferred route for synthesizing the compounds of the present invention involves several steps. The first step involves synthesizing Δ^2 -1,2,4-triazoline-5-thiones having the structure previously given as (II). Such compounds may be synthesized in accordance with one or more of the following equations:

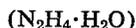


For given substituents R_1 and R_2 each of the above methods will give a different yield. Selection of the preferred method, consequently, is an empirical decision based on experience with given substituents. For example, R_1 substituents may include radicals such as trifluoromethyl, difluoromethyl, pentafluoroethyl, 2-trifluoromethylpropyl, chlorodifluoromethyl and the like. The R_2 substituents may include radicals such as methyl, ethyl, butyl, hexyl, heptyl and the like. The choice of the suitable

3

method will become obvious to those skilled in the art from the teachings herein set forth.

The particular carboxylic acids used in the above methods are commercially available or can be made by known methods. The thiosemicarbazides are, similarly, either available or can be synthesized by standard methods such as for example, the reaction of hydrazine hydrate



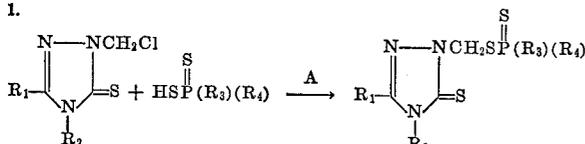
with an appropriate isothiocyanate (R_2NCS).

The compounds having the Structure (II) may be reacted with aldehydes such as formaldehyde, acetaldehyde, propionaldehyde and the like to obtain the compounds of Structure (III), e.g. 1-hydroxymethyl-4-methyl-3-trifluoromethyl- Δ^2 -1,2,4-triazoline-5-thione.

The hydroxymethyl derivatives may be reacted with compounds such as thionyl chloride, phosphorous pentachloride, phosphorous tribromide and the like to obtain the compounds of Structure (IV), e.g. 1-chloromethyl-4-methyl-3-trifluoromethyl- Δ^2 -1,2,4-triazoline-5-thione. The above synthesis is generally carried out in an inert organic solvent such as benzene, chloroform and the like at temperatures of less than 70° C. in an inert atmosphere such as nitrogen.

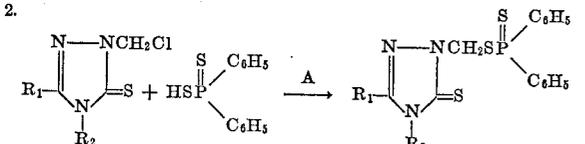
The final products of Structure I may be produced from, for example, 1-hydroxymethyl-4-methyl-3-haloalkyl- Δ^2 -1,2,4-triazoline-5-thiones (Structure III) or corresponding 1-halomethyl compounds (Structure IV) by employing various methods known in the art. Examples of some such methods are as follows:

1.



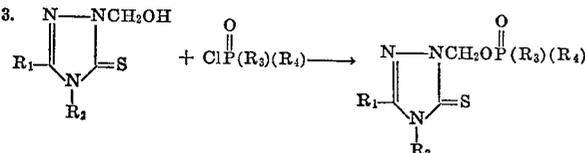
wherein R_3 and R_4 are independently alkyl, alkylamino, alkoxy or phenyl

2.



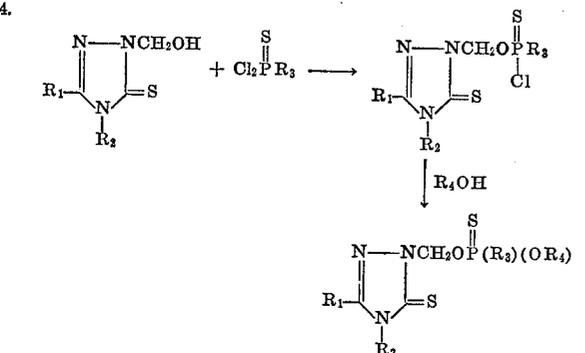
A represents acid binding agents, e.g. Na_2CO_3 , Et_3N , pyridine etc. Salts of the acids e.g. ammonium, sodium, potassium, etc., rather than the free acids, may also be used in the above reactions.

3.



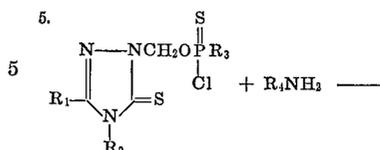
wherein R_3 and R_4 are independently alkyl, alkylamino, alkoxy or phenyl

4.

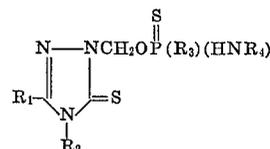


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wherein R_3 is alkyl, alkylamino, alkoxy or phenyl R_4 is alkyl



10

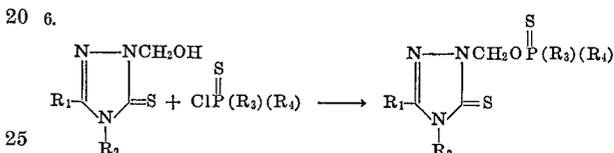


15

wherein

R_3 is alkyl, alkylamino, alkoxy or phenyl
 R_4 is alkyl

20



25

wherein R_3 and R_4 are alkoxy.

The above reactions can be carried out in water or organic solvents such as, for example, benzene, methanol, ethanol, acetone, butanone, ethyl acetate and the like at from about room temperature to about 80° C.

It has been found that the compounds of the invention having the Structure (I) are particularly distinguished by the presence of a fluoroalkyl or chlorodifluoromethyl group in the 3 position of the particular phosphate derivatives of Δ^2 -1,2,4-triazoline compounds. Such compounds have exhibited excellent insecticidal and acaricidal properties. Certain of the compounds show excellent ovicidal properties, whereas somewhat related compounds currently known in the art are absent such activity. Certain members of the Structure (I) compounds of the present invention have relatively high LD_{50} values and yet exhibit excellent insecticidal and acaricidal properties.

The compounds of the invention having the Structure (I) may be formulated in a variety of ways and concentrations for the purpose of employing them for insecticidal and/or acaricidal purposes. It is recognized that the particular type and concentration of formulation, as well as the mode of application of the active ingredient may control its biological activity in a given application.

Compounds of the invention may be prepared as simple solutions of the active ingredient in an appropriate solvent in which it is completely soluble at the desired concentration. Such solvent systems include water, alcohols, acetone, and other organic solvents. These simple solutions may be further modified by the addition of various surfactants, emulsifying or dispersing agents, colorants, odorants, anti-foaming agents, other pesticides or dormant oils which supplement or synergize the activity of the pesticides of the invention, or other adjuvants for any given application where deemed desirable to impart a particular type of biological response.

Compounds of the invention may also be formulated in various other types of formulations commonly recognized by those skilled in the art of agricultural or industrial chemicals. These formulations include, for example, compositions containing the active ingredient as granules of relatively large particle size, powder dusts, as wettable powders, as emulsifiable concentrates, as aerosol spray formulations, or as a constituent part of any other known type of formulation commonly utilized by those skilled in the art. Such formulations include the adjuvants and carriers normally employed for facilitating the dispersion of active ingredient for agricultural and industrial applications of pesticidal chemicals. These formulations may

5

contain as little as 0.25% or more than 95% by weight of the active ingredient.

Dust formulations are prepared by mixing the active ingredient with finely divided solids which act as dispersants and carriers for the ingredient in applying it to the locus of application for the desired control. Typical solids which may be utilized in preparing dust formulations of the active ingredients of the invention include talc, kieselguhr, finely divided clay, fullers' earth, or other common organic or inorganic solids. Solids utilized in preparing dust formulations of the active ingredient normally have a particle size of 50 microns or less. The active ingredient of these dust formulations is present commonly from as little as 0.25% to as much as 30% or more by weight of the composition. Granular formulations of the active ingredients are prepared by impregnating or adsorbing the toxicant on or into relatively coarse particles of inert solids such as sand, attapulgite clay, gypsum, corn cobs or other inorganic or organic solids. The active ingredient of these granular formulations is commonly present from 1.0% to as much as 20% or more by weight of the composition.

Wettable powder formulations are solid compositions of matter wherein the active ingredient is absorbed or adsorbed in or on a sorptive carrier such as finely divided clay, talc, gypsum, lime, wood flour, fullers' earth, kieselguhr, or the like. These formulations preferably were made to contain 50% to 80% of active ingredient. These wettable powder formulations commonly contain a small amount of wetting, dispersing or emulsifying agent to facilitate dispersion in water or other liquid carrier utilized to distribute the ingredient to the locus for the desired control.

Emulsifiable concentrate formulations are homogeneous liquid or paste compositions containing the active ingredient which will disperse in water or other liquid carrier to facilitate application of the ingredient to the locus for desired control. Such emulsifiable concentrate formulation of the active ingredients may contain only the active ingredient with a liquid or solid emulsifying agent or may contain other relatively nonvolatile organic solvents such as isophorone, dioxane, heavy aromatic naphthas, xylene, or dimethyl formamide. The active ingredient in such formulations commonly comprises 10.0% to 70.0% by weight of the active ingredient.

Aerosol spray formulations of the toxicants may be prepared wherein the active ingredient is dispersed in a finely divided form as a result of vaporization of a low boiling dispersant solvent carrier such as Freons.

The compounds of the present invention having the Structure (I) are compatible with other pesticides, bactericides, fungicides and the like to obtain desired biological activity.

The following examples are illustrative of the present invention and are not intended to limit the scope thereof.

EXAMPLES

(I) Synthesis of intermediate compounds

EXAMPLE 1

(a) A solution containing four grams of 4-methyl-1-trifluoroacetylthiosemicarbazide and 30 mls. of a 10% aqueous sodium carbonate solution was refluxed for about 2 hours. The mixture was cooled to about 10° C. and acidified with hydrochloric acid to yield a solid crude product. The crude product was recrystallized from a methylene chloride-petroleum ether medium to provide a final product having a melting point of 119–120° C. The final product was identified as 4-methyl-3-trifluoromethyl- Δ^2 -1,2,4-triazoline-5-thione.

$C_4H_4N_3SF_3$ —Required (percent): C, 26.25; H, 2.20; N, 22.96. Found (percent): C, 25.90; H, 2.16; N, 22.92.

(b) Ten and one-half grams of 4-methyl-thiosemicarbazide were placed into a solution containing 100 mls. of xylene and 10.6 gms. of difluoroacetic acid and the

6

resulting suspension refluxed under a Dean-Stark trap until water ceased to be obtained. The reaction mixture was cooled to about 12° C. and filtered to yield 13.5 gms. of a product having a melting point of 171–174° C. The resulting product was identified as 3-difluoromethyl-4-methyl- Δ^2 -1,2,4-triazoline-5-thione.

$C_4H_3N_3SF_2$ —Required (percent): C, 29.09; H, 3.05; N, 25.44. Found (percent): C, 29.46; H, 3.11; N, 25.73. Further compounds of the Structure (II), listed in the following table, are prepared in accordance with the above procedures:

No.	R ₁	R ₂
1.....	CF ₃	C ₂ H ₅
2.....	CHF ₂	C ₄ H ₉
3.....	C ₂ F ₅	CH ₃
4.....	CH ₃ CHCH ₂ — CF ₃	CH ₃
5.....	CClF ₂	CH ₃

EXAMPLE 2

(a) Twenty grams of the compound as produced in accordance with the procedure of Example 1(a) and 21 gms. of a 37% aqueous solution of formaldehyde were heated together at a temperature of 60° C. about 1 hour at which time a complete solution was obtained. The reaction mixture was concentrated under vacuum and the residue dissolved in 100 mls. of ethyl acetate. The ethyl acetate solution was dried over anhydrous sodium sulfate and concentrated under vacuum to yield an oil which solidified to wax on standing. The product recovered (21 gms.) was identified as 1-hydroxymethyl-4-methyl-3-trifluoromethyl- Δ^2 -1,2,4-triazoline-5-thione.

Further compounds of the Structure (III), listed in the following table are prepared in accordance with the above procedures

No.	R ₁	R ₂
1.....	CF ₃	C ₂ H ₅
2.....	CHF ₂	CH ₃
3.....	CHF ₂	C ₄ H ₉
4.....	C ₂ F ₅	CH ₃
5.....	CH ₃ CHCH ₂ — CF ₃	CH ₃
6.....	CClF ₂	CH ₃

EXAMPLE 3

(a) Twenty-one grams of the product produced in Example 2 was admixed in a round bottom flask with a mixture of 53 mls. of benzene and 25.6 mls. of thionyl chloride, said mixture having been previously cooled to about 5° C. by means of an ice bath. The total mixture was obtained in a nitrogen atmosphere. Nitrogen was bubbled through the resulting mixture until there was no evolution of hydrogen chloride gas. The reaction mixture was subsequently concentrated under vacuum. The resulting product (21 gms.) was crystallized from petroleum ether and the melting point was determined to be 40–43° C. The product recovered was identified to be 1-chloromethyl-4-methyl-3-trifluoromethyl- Δ^2 -1,2,4-triazoline-5-thione.

$C_5H_4ClF_3N_3S$ —Required (percent): C, 25.88; H, 2.17; N, 18.11. Found (percent): C, 26.01; H, 2.33; N, 18.16.

7

Further compounds of the Structure (IV), listed in the following table are prepared in accordance with the above procedures

No.	R ₁	R ₂
1.....	CF ₃	C ₂ H ₅
2.....	CHF ₂	CH ₃
3.....	CHF ₂	C ₂ H ₅
4.....	C ₂ F ₅	CH ₃
5.....	CH ₃	CH ₃
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CHCH}_2- \\ \\ \text{CF}_3 \end{array}$	
6.....	CClF ₂	CH ₃

(II) Synthesis of compositions of Structure (I) from intermediates

EXAMPLE 4

(1) Four grams of the product produced in Example 3(a) and 3.5 gms. of ammonium diethyldithiophosphate were refluxed in 200 mls. of acetone for about 3 hours. The reaction mixture was cooled to about 10° C. filtered and the filtrate concentrated under vacuum to an oil which solidified on cooling to room temperature. The resulting product was crystallized from aqueous methanol to produce 5 gms. of a product having a melting point of 88-90° C. The product recovered was identified to be 1-diethoxyphosphinothioylmethyl - 4 - methyl-3-trifluoromethyl-Δ²-1,2,4-triazoline-5[4H]-thione.

C₉H₁₅N₃F₃O₂S₃P.—Required (percent): C, 28.37; H, 3.97; N, 11.03. Found (percent): C, 28.58; H, 3.90; N, 11.00.

Further compounds of the Structure (I), listed in the following table are prepared in accordance with the above procedures.

No.	R ₁	R ₂	R ₃	R ₄
2.....	CF ₃	C ₂ H ₅	OC ₂ H ₅	OC ₂ H ₅
3.....	CF ₃	CH ₃	OC ₂ H ₅	OC ₂ H ₅
4.....	CF ₃	CH ₃	i-OC ₂ H ₇	i-OC ₂ H ₇
5.....	C ₂ F ₅	CH ₃	OC ₂ H ₅	OC ₂ H ₅
6.....	C ₂ F ₅	CH ₃	OC ₂ H ₅	OC ₂ H ₅
7.....	CHF ₂	CH ₃	OC ₂ H ₅	OC ₂ H ₅
8.....	CHF ₂	C ₂ H ₅	OC ₂ H ₅	OC ₂ H ₅
9.....	CH ₃	CH ₃	OC ₂ H ₅	OC ₂ H ₅
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CHCH}_2- \\ \\ \text{CF}_3 \end{array}$			
10.....	CClF ₂	CH ₃	OC ₂ H ₅	OC ₂ H ₅

EXAMPLE 5

A mixture of 10.0 gms. of the product produced in Example 3(a), 11.0 gms. of diphenylphosphinodithioic acid [(C₆H₅)₂PSSH] and 4.4 gms. of triethylamine in benzene was refluxed for three hours. The solids were filtered from the cooled reaction mixture and the benzene filtrate concentrated, under vacuum to an oil. The oil was crystallized from benzene-light petroleum mixture to give a product identified to be 1-diphenylphosphinothioylmethyl-4-methyl - 3 - trifluoromethyl-Δ²-1,2,4-triazoline-5[4H]-thione, which had a melting point of 123-126° C.

EXAMPLE 6

A mixture of 8.0 gms. of the product produced in Example 2(a), 6.6 gms. of ethyl phosphorochloridate [(C₂H₅O)₂POCl] and 5.2 mls. of triethylamine in benzene was refluxed for three hours and then allowed to stir at room temperature overnight. The solids were filtered off and the filtrate concentrated to an oil. The oil was washed with a 2% aqueous sodium carbonate solution and the residue extracted with diethyl ether. The ether extract was dried over anhydrous sodium sulphate and concentrated to a residual oil which was identified to be 1-diethoxyphosphinomethyl-4-methyl - 3 - trifluoromethyl-Δ²-1,2,4-triazoline-5[4H]-thione,

8

EXAMPLE 7

A mixture of 8.0 gms. of the product produced in Example 2(a), 4.2 gms. of ethyl phosphorochloridate [(C₂H₅O)₂PSCl] and 5.4 mls. of triethylamine was refluxed in benzene for three hours and then allowed to stir at room temperature overnight. The insolubles were filtered off and the filtrate concentrated to an oil. The oil was washed with a 2% aqueous sodium carbonate mixture and the insolubles extracted with diethyl ether. The ether was dried over anhydrous sodium sulphate and concentrated to a residual oil which was identified to be 1-diethoxyphosphinothioylmethyl-4-methyl - 3 - trifluoromethyl-Δ²-1,2,4-triazoline-5[4H]-thione.

EXAMPLE 8

A mixture of 6.0 gms. of the product produced in Example 2(a), 4.6 gms. of ethylphosphorodichloridate [(C₂H₅)₂PSCl₂] and 4 mls. of triethylamine in 100 mls. of benzene was stirred at room temperature overnight. The insolubles were filtered off and the filtrate concentrated to a residual oil which was washed with a 2% aqueous sodium carbonate solution. The residue was extracted with ether, the ether extract dried over anhydrous sodium sulphate and concentrated to a residual oil.

A mixture containing the reaction produced above (5.2 gms.), absolute ethanol (0.7 gms.) and triethylamine (1.5 gms.) was refluxed in 50 mls. of benzene for three hours. The cooled reaction mixture was filtered and the filtrate concentrated to a residual oil which was washed with a 2% aqueous sodium carbonate solution. The residue was extracted with diethyl ether, the diethyl ether dried over anhydrous sodium sulphate and was then concentrated to an oil which was identified to be 1-ethoxy-1-ethylphosphinylthioylmethyl - 4 - methyl-3-trifluoromethyl-Δ²-1,2,4-triazoline-5[4H]-thione.

(III) Insecticidal and acaricidal activity

Various compounds of Example 4 and those of other examples having the Structure (I) were tested for biological activity for controlling a variety of insects and acarids. The following discussion sets forth the method employed to conduct tests on specific pests and the corresponding tables include the results obtained therefrom. Such tests and results are illustrative only and are not intended to limit the scope of the biological activity of various compounds having the Structure (I).

(A) Tests conducted with the Mexican Bean Beetle

The compounds were dissolved in acetone and diluted to appropriate concentrations in de-ionized water containing suitable wetting and emulsifying agents. Foliar portions of cranberry bean plants in first true leaf growth stage were dipped into an agitated test solution containing a specific compound, allowed to air dry and placed on holding racks provided with a subterranean water source. Three test plants were used for each chemical dilution.

After the plants were dried, ten (10) third-instar larvae of the Mexican Bean Beetle (*Epilachna varivestis*) were caged on the tested plants for a period of forty-eight (48) hours. Observations for insect mortality were made at the end of the forty-eight (48) hour period. The results are set forth in Table I below.

TABLE I

Concentration, p.p.m.	Percent mortality						
	500	250	100	50	25	10	5
Compound of Example Number:							
4-1.....	100	100	100	100	100	100	100
4-2.....	100	100	100	100	40	13	-----
4-3.....	100	100	100	100	100	100	73
4-4.....	100	100	100	100	100	80	27
4-5.....	100	100	100	87	80	20	-----
4-6.....	100	100	100	100	100	80	27
4-7.....	-----	-----	-----	-----	-----	100	100
4-10.....	100	100	100	100	100	100	100
7.....	100	87	20	7	-----	-----	-----

(B) Tests conducted with the Southern Army Worm

The procedure described in A above was substantially repeated to determine the toxicity of the compounds against the Southern Army Worm. The results of such tests are set forth in Table II below.

TABLE II

Concentration, p.p.m.	Percent mortality				
	1,000	500	250	200	100
Compound of Example Number:					
4-1	100	100	100	90	50
4-2	87				
4-3	100	93	27		0
4-4	20	7	0		0
4-5	40	27	13		0
4-6	100	93	27		0
4-7				100	38

(C) Tests conducted with the Pea Aphid

Chemical solutions were prepared as described in A above. Adult Pea Aphids (*Macrosiphum pisi*) enclosed in wire mesh containers were sprayed with the chemical solutions for a period of about five (5) seconds and subsequently transferred to untreated Windsor broad bean plants using ten (10) aphids per plant and three plants per chemical treatments. Insect mortality was determined forty-eight (48) hours after chemical treatment. The results are set forth in Table III below.

TABLE III

Concentration, p.p.m.	Percent mortality						
	500	250	25	50	25	10	5
Compound of Example Number:							
4-1	100	100	100	57	97	10	
4-2	100	100	100	100	40	23	
4-3	96	96	96	93	96	88	90
4-4	100	87	87	90	84	100	43
4-5	100	100	93	93	93	13	
4-6	100	93	83	33			
4-7					95	80	
4-10	90	80	80	30		13	

(D) Test conducted with acarids

Chemical test solutions were prepared as described in A above. Cranberry bean plants infested with mixed life stages of two-spotted spider mites (*Tetranychus telarius*) were dipped into the chemical solutions. The plants were air dried and subsequently placed on holding racks provided with a subterranean water source. Three test plants were used for each chemical treatment. Forty-eight (48) hours after chemical treatment mite mortality was observed. The results are set forth in Table IV below.

TABLE IV

Concentration, p.p.m.	Percent mortality						
	500	250	125	60	25	10	5
Compound of Example Number:							
4-1	100	100	100	100	100	91	68
4-2	100	100	100	100	89	50	
4-3	100	100	100	100	93	97	96
4-4	100	100	100	100	93	83	81
4-5	100	100	100	100	54	50	50
4-6	100	100	100	100	77	36	11
4-7					100		96
4-10	100	100	100	100		100	74
5	79	43	36				
6	55	53	19				
7	100	100	71	48		15	
8	37	23	20				

(E) Tests for residual toxicity

Representative compounds, having the Structure (I) and prepared as described in Example 4, were tested for residual toxicity of chemical deposit of foliage of treated plants. Chemical solutions of the compounds were prepared and applied in accordance with the procedures described in A above. The larvae of the Mexican Bean Beetle were employed in the particular tests. Insect mortality was determined seventy-two (72) hours after the larvae were introduced and caged on the treated foliage. The table shows the degree of activity against the larvae at various time intervals after initial treatment of the foliage. The results are set forth in Table V below.

TABLE V

P.p.m.	Percent mortality (72 hours)					
	Age of residue					
	0 day	4 days	7 days	15 days	22 days	27 days
Compound of Example Number:						
4-1	2	100	100			
4-1	10	100		100	100	5
4-7	2	100	100			
4-7	10	100		100		100

(F) Systemic insecticidal activity

Cranberry bean plants in the first true leaf growth stage and in soil of low moisture content were treated with 20 mls. of an aqueous solution of a compound having the Structure (I), said solution being applied as a surface drench. All treatments were applied in triplicate. Twenty-four (24) hours after such application, the plants were subjected to continuous subterranean watering for seventy-two (72) hours. Forty-eight (48) hours after application of the solution to the soil, adult Pea Aphids were transferred to and caged on the foliar portions of the plants for a period of forty-eight (48) hours. Insect mortality was observed seventy-two (72) hours after the insects were exposed to feeding on the foliage. The results are set forth in Table VI below.

TABLE VI

Concentration, p.p.m.	Percent mortality (72 hours)		
	25	10	5
Compound of Example Number:			
4-1	100	40	0
4-7		100	

(G) Ovicidal activity

Certain of the compositions have also shown highly desirable results as an ovicide. Liquid compositions prepared as described above were contacted with a foliar surface having the eggs of various insects and mites attached thereto at concentrations set forth in the table below. "Ovicidal" indicates the percent of total eggs that did not hatch. "Residual" indicates the percent of emerged young that died upon contact with the treated foliar surface. The results were taken after a six (6) day exposure of the eggs and emerged young to the compositions. The compositions identification "No." is taken from Example 4.

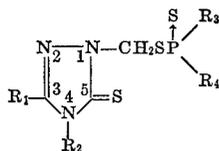
Number:	Percent control		
	P.p.m.	Ovicidal	Residual
4-1	25	100	
4-7	25	50	95
4-10	125	100	

From the results shown in the tables above, it can readily be seen that compositions of the present invention having the Structure (I) generally show excellent insecticidal and acaricidal properties.

11

What is claimed is:

1. A composition having the general structure:



wherein

R₁ represents fluoroalkyl radicals having from 1 to 7 carbon atoms or a chlorodifluoromethyl radical,

R₂ represents lower alkyl radicals having from 1 to 7 carbon atoms, and

R₃ and R₄ independently represent alkoxy radicals having from 1 to 7 carbon atoms.

2. The composition according to claim 1 wherein R₁ is trifluoromethyl, R₂ is methyl, and R₃ and R₄ are ethoxy.

3. The composition according to claim 1 wherein R₁ is trifluoromethyl, R₂ is ethyl, and R₃ and R₄ are ethoxy.

4. The composition according to claim 1 wherein R₁ is trifluoromethyl, R₂ is methyl, and R₃ and R₄ are methoxy.

5. The composition according to claim 1 wherein R₁ is trifluoromethyl, R₂ is methyl, and R₃ and R₄ are isopropoxy.

6. The composition according to claim 1 wherein R₁ is pentafluoroethyl, R₂ is methyl, and R₃ and R₄ are methoxy.

12

7. The composition according to claim 1 wherein R₁ is pentafluoroethyl, R₂ is methyl, and R₃ and R₄ are ethoxy.

8. The composition according to claim 1 wherein R₁ is difluoromethyl, R₂ is methyl, and R₃ and R₄ are ethoxy.

9. The composition according to claim 1 wherein R₁ is difluoromethyl, R₂ is butyl, and R₃ and R₄ are ethoxy.

10. The composition according to claim 1 wherein R₁ is 2-trifluoromethylpropyl, R₂ is methyl, and R₃ and R₄ are ethoxy.

11. The composition according to claim 1 wherein R₁ is chlorodifluoromethyl, R₂ is methyl, and R₃ and R₄ are ethoxy.

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