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PATENT SPECIFICATION

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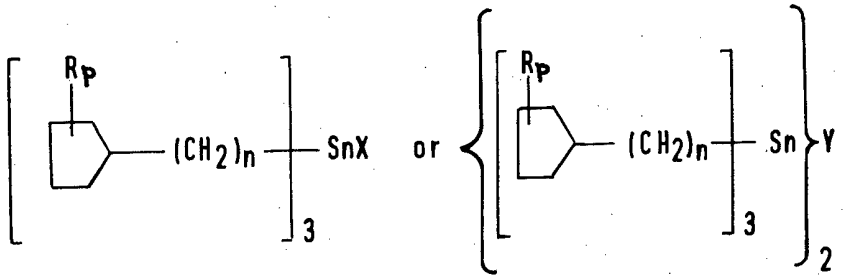
(54) NOVEL TRICYCLOPENTYLTIN COMPOUNDS AND PESTICIDAL COMPOSITIONS CONTAINING SAME

(71) We, M & T CHEMICALS INC., a corporation organised and existing under the laws of the State of Delaware, United States of America, with executive offices at American Lane, Greenwich, Conneticut, U.S.A., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

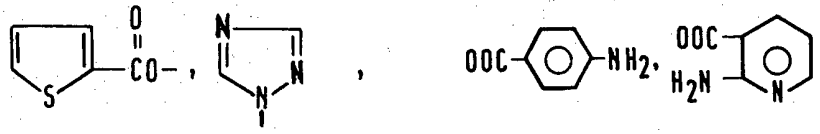
Fungi and pestiferous insects, including mites, are responsible for a considerable portion of the annual damage to agricultural crops. Many trialkyltin derivatives, particularly tri - n - butyltin and tri - n - amyltin derivatives, are capable of controlling these organisms but are insufficiently selective towards plant crops, in that while the fungus or insect attacking the plant may be controlled the plant to which the organotin compound is applied may be killed or severely damaged. Moreover, many triorganotin compounds are active against either fungi or insects but not against both of these classes or organism.

It is therefore an object of this invention to provide a class of triorganotin compounds that can effectively control both fungi and insects on living plants without significantly damaging the plant. Surprisingly it has been found that certain triorganotin compounds wherein the hydrocarbon groups bonded to the tin atom contain a cyclopentyl structure can fulfil this object.

This invention provides novel triorganotin compounds of formula



wherein R is an alkyl group containing from 1 to 3 carbon atoms, n is 0, 1 or 2 and p is 0 or 1, with the proviso that at least one of n and p is always 0, and then when n and p are both 0, X represents fluorine, nitrate, cyanate, thiocyanate, carbamoyloxy, thiocarbamoyloxy, carboxylate (—OOCR¹) other than acetoxy, dithiocarbamoyl, alkoxy (OR¹), phenoxy, thiophenoxy, mercaptide, (—SR¹),



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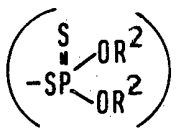
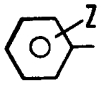
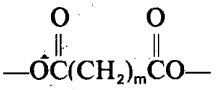


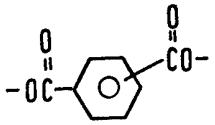
R^1 being an alkyl group containing from 1 to 12 carbon atoms and R^2 being an alkyl group containing from 1 to 12 carbon atoms or a phenyl group,



wherein Z is hydrogen, halogen, an alkyl or alkoxy group containing from 1 to 3 carbon atoms or nitro and Y is



m being an integer from 2 to 10 inclusive,



sulphur sulphate or carbonate; with the proviso that when either n or p is not 0, X also represents hydroxyl or acetoxy and Y also represents oxygen.

These compounds are particularly effective as control agents for fungi and insects and nevertheless do not exhibit the high level of phytotoxicity characteristic of tri - n - alkyltin compounds. This is also true of tri - phenyltin hydroxide, chloride, bromide and acetate which, although known per se have not been previously known to have insecticidal and fungicidal activity.

The invention includes a composition for killing fungi and insects, which consists essentially of an inert liquid or solid carrier and a fungicidally and insecticidally effective amount of a triorganotin compound of either of the above formulae or of tricyclopentyltin hydroxide, chloride, bromide or acetate.

Tri(cyclopentyl)tin and tri(cyclopentylalkyl)tin halides wherein the halogen is chlorine or bromine can be prepared by reacting at least three moles of the corresponding cyclopentyl or cyclopentylalkyl magnesium halide, $CypMgZ^1$ or $Cyp(CH_2)_nZ^1$, wherein Cyp represents a cyclopentyl ring, with one mole of an alkyltin trihalide $R^3SnZ^2_3$ wherein R^3 is an alkyl group containing 1 to 4 carbon atoms. The resultant tetraorganotin compound, Cyp_3SnR^3, is then reacted with an equimolar amount of a stannic halide, SnZ^3_4. During this reaction the alkyl group R^3 in the tetraorganotin compound is replaced by a halogen atom from the stannic halide. The reactions involved are represented by the following two equations where Z^1, Z^2 and Z^3 represent chlorine or bromine.

$$3CypMgZ^1+R^3SnZ^2_3 \quad Cyp_3SnR^3+3MgZ^1Z^2$$
$$Cyp_3SnR^3+SnZ^3_4 \quad Cyp_3SnZ^3+R^3SnZ^3_3$$

The aforementioned alkyltin trihalide $R^3SnZ^2_3$ can, in turn, be prepared by reacting the corresponding alkyl halide, R^3Z^2, with a stannous halide SnZ^2_2 as described in United States Patent 3,340,283.

The reaction between the stannic halide and the tetraorganotin compound should be performed under anhydrous conditions at a temperature of –25 to 80°C, preferably +25 to 80°C., in a hydrocarbon solvent. Preferred solvents include pentane, hexane and cyclohexane.

Preferably the stannic halide is dissolved in an organic solvent and the resultant solution added dropwise to a second solution containing the tetraorganotin compound in the same solvent. The temperature of the reaction mixture is preferably maintained below 30°C, during the addition, which requires about one hour, after which the mixture is heated to a temperature of 35 to 80°C. Preferably the temperature employed is the reflux temperature of the reaction mixture. Heating is continued for 15 to 60 minutes to ensure complete reaction. The reaction mixture is then allowed to cool to ambient temperature, and extracted with one or more portions of water or aqueous mineral acid. The by-product of the reaction, a monoorganotin trihalide, $R^3SnZ^3_3$, is soluble in the aqueous phase of the reaction mixture. The desired product remains

in the organic phase, and may readily be isolated by boiling off the hydrocarbon solvent. No further purification is usually required, but the product can be distilled if desired. The organic layer is preferably freed of any dissolved water following the extracting step. Any of the conventional chemical dehydrating agents are suitable, provided that they do not react with either the triorganotin halide or the hydrocarbon solvent. Preferred dehydrating agents include anhydrous magnesium sulphate, anhydrous sodium sulphate and anhydrous calcium sulphate.

Tri(cyclopentylalkyl)tin bromides can be prepared by the gradual addition of bromine to a solution containing the corresponding tetra(cyclopentylalkyl)tin compound. The tetraorganotin compound is, in turn, prepared by reacting a cyclopentylalkyl magnesium halide with a stannic halide in a molar ratio of 4:1, respectively.

The triorganotin chlorides, bromides and iodides can be converted into compounds of the above formulae by reaction with the reagents indicated in the following table:—

Organotin Derivative	+ Reagent	Desired Product
chloride, bromide or iodide	carboxylic acid+ acid acceptor, e.g. an amine	carboxylate, e.g. acetate
chloride, bromide or iodide	alkali metal salt of a carboxylic acid	carboxylate, e.g. acetate
chloride, bromide or iodide	aqueous solution of alkali metal hydroxide	oxide (or hydroxide)
chloride, bromide or iodide	alkalimetal alkoxide or alcohol+acid acceptor (e.g. an amine)	alkoxide
chloride, bromide or iodide	alkali metal phenoxide or phenol+acid acceptor	phenoxide
chloride, bromide or iodide	potassium fluoride or hydrofluoric acid	fluoride
chloride, bromide or iodide	alkali metal sulphide	sulphide
chloride, bromide or iodide	alkali metal sulphate	sulphate
chloride, bromide or iodide	mercaptan+acid acceptor	mercaptide
chloride, bromide or iodide	alkali metal cyanate	cyanate
chloride, bromide or iodide	alkali metal thiocyanate	thiocyanate
chloride, bromide or iodide	alkali metal thiocarbamate	thiocarbamate
chloride, bromide or iodide	alkali metal dithiocarbamate	dithiocarbamate
chloride, bromide or iodide	phosphoric acid or alkali metal phosphate	phosphate
chloride, bromide or iodide	alkali metal dialkyldithio-phosphate	dialkyldithio-phosphate
oxide or hydroxide	carboxylic acid or anhydride	carboxylate
oxide or hydroxide	alcohol (or phenol)	alkoxide (or phenoxide)
oxide or hydroxide	hydrofluoric acid	fluoride
oxide or hydroxide	dilute (10—25 weight %) aqueous sulphuric acid	sulphate
oxide or hydroxide	hydrogen sulphide	sulphide
oxide or hydroxide	alkyl or aryl mercaptan	mercaptide
oxide or hydroxide	carbondioxide	carbonate
hydroxide	heat to remove water	oxide

The reaction conditions such as preferred solvents, temperatures and reaction times for preparing the derivatives summarized in the preceding table are known in the art and, therefore, do not require a detail description in the present specification. A comprehensive treatment of this subject matter together with numerous literature references is contained in an article by R. K. Ingham et al. that appeared in the October, 1960 issue of Chemical Reviews (pp. 459—539). The aforementioned derivatives are liquids or solids at ambient temperature, depending upon the substituents represented by X or Y.

The tricyclopentyltin and tricyclopentylalkyltin compounds according to the invention effectively control many types of undesirable fungi and insects, particularly mites, when applied to living plants that are susceptible to infestations of these organisms. The combination of fungicidal and miticidal activity is not common for a single organotin compound. A single application of these compounds to living plants or other substrates provides residual and extended control of many varieties of fungi and insects for a considerable period of time, the duration of which is dependent to some extent upon mechanical and biological influences, including weather. Formulations containing the present organotin compounds can be applied directly to the organism to be controlled.

In preparing compositions for application to plants the organotin compound is often augmented or modified by combining it with one or more commonly employed pesticide additives or adjuvants including organic solvents, water or other liquid carriers, surfactants to aid in dispersing or emulsifying the organotin compound and finely comminuted solid carriers. Depending upon the concentration of triorganotin compound in these compositions, they can be employed either without additional diluents or as liquid concentrates which are subsequently diluted with one or more additional inert liquids to produce the ultimate treating compositions. In compositions employed as concentrates, the triorganotin compound can be present at concentration of 5 to 98% by weight. Other biologically active agents that are chemically compatible with the triorganotin compounds can also be added.

The optimum effective concentration of tin compound to be employed as toxicant in a composition is dependant upon whether the organism is contacted with or, as in the case of insects, ingests the toxicant. The actual weight of compound constituting an effective dose is primarily dependent upon the susceptibility of the particular organism to a given triorganotin compound. For control of insects good results are obtained with liquid or dust compositions containing as little as one part per million by weight of toxicant. Compositions containing up to 90 percent by weight of toxicant can be employed to treat a heavily infested area.

In the preparation of dust compositions, the organotin compound can be blended with many commonly employed finely divided solid carriers such as fuller's earth, attapulgite, bentonite, pyrophyllite, vermiculite, diatomaceous earth, talc, chalk, gypsum and wood flour. The carrier, usually in a finely divided form, is ground or mixed with the toxicant or wetted with a dispersion of the toxicant in a volatile liquid. Depending upon the relative proportions of toxicant and carrier, these compositions can be employed as concentrates that are subsequently diluted with additional solid carrier to obtain the desired amount of active ingredient. Alternatively, such concentrate dust compositions can be employed in combination with various known anionic, cationic or non-ionic surfactants as emulsifying or dispersing agents to form spray concentrates. Such concentrates are readily dispersible in liquid carriers to form spray compositions or liquid formulations containing the toxicants in any desired amount. The choice and concentration of surfactant are determined by the ability of the material to facilitate the dispersing of the concentrate in the liquid carrier to produce the desired liquid composition. Suitable liquid carriers include water, methanol, ethanol, isopropanol, methyl ethyl ketone, acetone, methylene chloride, chlorobenzene, toluene, xylene and petroleum distillates. Among the preferred petroleum distillates are those boiling under 400°F at atmospheric pressure and having a flash point above 80°F.

Liquid compositions can also be prepared by dissolving one of the triorganotin compounds in a mixture containing a water-immiscible organic liquid and a surface active dispersing agent. The resultant emulsifiable concentrate is then further diluted with water and an oil to form spray mixtures in the form of oil-in-water emulsions. In such compositions, the carrier comprises an aqueous emulsion, i.e. a mixture of water-immiscible solvent, emulsifying agent and water. Preferred

dispersing agents for these compositions are oil-soluble and include the condensation products of alkylene oxides with phenols and organic and inorganic acids, polyoxyethylene derivatives of sorbitan esters, alkylarylsulphonates, complex ether alcohols and mahogany soaps. Suitable organic liquids to be employed in the compositions include petroleum distillates, hexanol, liquid halohydrocarbons and synthetic organic oils. The surface active dispersing agents are usually employed in the liquid dispersions and aqueous emulsions in the amount of 1 to 20 percent by weight of the combined weight of the dispersing agent and the active toxicant.

When operating in accordance with the present invention, the organotin compound or a composition containing the compound can be applied directly onto the organism to be controlled or to the site to be protected, particularly plants and trees. Application to the foliage of plants is conveniently carried out using power dusters, boom sprayers and spray dusters. When employed in this manner the compositions should not contain any significant amounts of phytotoxic diluents. In large scale operations, dusts or low volume sprays may be applied from an aircraft.

In the following Examples all parts and percentages are by weight unless otherwise specified.

EXAMPLES

EXAMPLE 1

Preparation of Tricyclopentyltin Chloride and Derivatives Thereof

A. Preparation of Butyltricyclopentyltin

To 24.3 g (1 g atom) of magnesium chips heated to a temperature of 40°C under a nitrogen atmosphere was added a 25 cc portion of a solution containing 149 g (1 mole) of bromocyclopentane dissolved in 750 cc of anhydrous tetrahydrofuran. The reaction was initiated using a few drops of ethylene dibromide. The remaining portion of the bromocyclopentane solution was gradually added during a period of 2 hours while the reaction mixture was heated to the boiling point. Heating was continued for an additional 1.5 hours, during which time 15 cc of a 3 normal solution of butylmagnesium bromide in tetrahydrofuran was added to react with any impurities which could prevent or inhibit the formation of cyclopentylmagnesium bromide. A small particle of iodine was also added as an initiator for the reaction. The reaction mixture was allowed to cool to ambient temperature and remain at this temperature for 16 hours, during which time stirring of the mixture was continued. At the end of this period all of the magnesium appeared to have reacted. A 100 cc portion of tetrahydrofuran was added to compensate for solvent loss resulting from evaporation, after which the reaction mixture was heated to the boiling point for two hours. A 500 cc portion of this solution containing 0.66 mole of cyclopentyl magnesium bromide was added dropwise to a stirred solution of butyltin trichloride (56.4 g, 0.2 mole) dissolved in 250 cc of dry benzene. The addition required one hour and was conducted under a nitrogen atmosphere. During the addition the temperature of the reaction mixture was maintained below 45°C. Following completion of the addition the reaction mixture was heated to the boiling point for one hour, then allowed to cool to ambient temperature and stirred for 18 hours. To the resultant mixture was added a solution of 35 g of citric acid in 200 cc of water. The organic phase of the resultant two phase liquid was separated and the water present therein removed by addition of anhydrous magnesium sulphate, which was subsequently removed by filtration. The solvent was evaporated under reduced pressure to yield 72.25 g (94% yield) of a liquid, butyltricyclopentyltin, exhibiting a refractive index (η_D^{27}) of 1.5220. This liquid was extracted once with methanol. Analysis by vapor phase chromatography indicated that the product was 96.7% pure. The product was found to contain 30.24% tin. The calculated value for butyltricyclopentyltin is 30.98%.

B. Cleavage of Butyltricyclopentyltin to Tricyclopentyltin Chloride

A 19.2 g (0.05 mole) portion of the butyltricyclopentyltin prepared as described in part A of this Example was dissolved in 75 cc of heptane. To this solution was added a solution of 13.0 g (0.05 mole) of anhydrous stannic chloride in 75 cc heptane. The addition required 20 minutes, following which the resultant mixture was heated to the boiling point for 30 minutes and then allowed to cool to ambient temperature. A solution obtained by combining 4 cc of 12N aqueous hydrochloric acid and 96 cc water was then added to the reaction mixture with

vigorous stirring both during the addition and for five minutes thereafter. The organic layer of the resultant two-phase liquid was combined with an aqueous hydrochloric acid solution prepared as described hereinabove. The organic layer was isolated and the water therein removed by addition of anhydrous magnesium sulphate. The heptane was then evaporated under reduced pressure to yield 17.8 g of pale yellow crystals exhibiting a melting range of 41—44°C. Upon analysis by vapor phase chromatography the product was found to be 97.2% pure. Following a recrystallization from pentane at −78°C, the product melted between 44 and 45°C and was 99.6% pure, as determined by vapor phase chromatography.

Tricyclopentyltin hydroxide was prepared by adding a solution of the corresponding chloride (18.1 g of the chloride in 40 cc of tetrahydrofuran) to a solution containing 3.0 g of sodium hydroxide, 12 cc water and 12 cc methanol. The addition was gradual and required 20 minutes, at which time 12 cc of water were added. The resultant slurry was stirred for 0.5 hour, and 150 cc of water were then added to completely precipitate the product. The solid was isolated and washed with deionized water until no detectible amount of chloride ion was present in the water. The solid was then dried in a circulating air oven maintained at a temperature of 40°C. Analysis by potentiometric titration indicated that the hydroxide was between 98.6 and 99.1% pure.

C. Tricyclopentyltin Fluoride

Tricyclopentyltin fluoride was prepared from the corresponding hydroxide. A solution of 300 g of tricyclopentyltin hydroxide in 3600 cc of tetrahydrofuran was clarified by filtration. To this solution was gradually added a solution obtained by combining 50 g of a 48% aqueous hydrofluoric acid solution with 150 cc of water. The resultant mixture, which contained a white precipitate, was heated to the boiling point (64°C) for 0.25 hour, then cooled to ambient temperature filtered, and the precipitate was washed sequentially with 1 litre of a 0.1% aqueous hydrofluoric acid solution, 1 litre of deionized water and 500 cc methanol. After being dried under reduced pressure at a temperature of 50°C the white solid (280 g) melted from 275 to 280°C with evidence of decomposition. The solid was found to contain 34.05% tin and 5.32% fluorine. The calculated values for tri(cyclopentyl)tin fluoride are 34.40% tin and 5.51% fluorine.

D. Tricyclopentyltin Acetate

To a suspension of 17.15 g tricyclopentyltin hydroxide in 100 cc of diethyl ether was added dropwise over 0.25 hour, a solution of 3.15 g acetic acid (glacial) in 100 cc diethyl ether. The solids dissolved and the solution was stirred for 0.25 hour at 25°C. 15 g of anhydrous magnesium sulphate were added to the solution and the mixture was stirred for 1 hour to remove water formed during the reaction. The mixture was then filtered and the solvent was removed on a rotary evaporator to yield 20 g of a white solid. The solid was placed in a desiccator over sodium hydroxide pellets and held under reduced pressure for 48 hours to remove excess unreacted acetic acid. The product, a white solid, weighed 18.7 g and melted from 52 to 54°C.

Analysis:	Found:	Tin, 30.65%; Acid No. 160
	Calculated:	Tin, 30.82%; Acid No. 146

E. Tricyclopentyltin 2-ethylhexanoate

A 17.1 g portion of tricyclopentyltin hydroxide and 7.2 g of 2 - ethylhexanoic acid in 200 cc benzene was heated to the boiling point and the by-product water (0.84 cc) was removed using a Dean-Stark trap. The benzene was evaporated under reduced pressure to yield 23.5 g of a yellow liquid, $\eta_D^{27}=1.5068$.

Analysis:	Found:	Sn, 25.14%; Acid No. 123.6
	Calculated:	Sn, 25.29%; Acid No. 119.5

F. Tricyclopentyltin Benzoate

The benzoate was prepared using the procedure described for the 2 - ethylhexanoate using 17.1 g tricyclopentyltin hydroxide and 6.1 g benzoic acid. The product, recrystallized once from n - hexane at −70°C, weighed 19.6 g and melted from 37 to 38.5°C.

Analysis:	Found:	Tin, 26.42%; Acid No. 131
	Calculated:	Tin, 26.54%; Acid No. 125

G. Bis[tricyclopentyltin] Oxide

By heating a sample of the hydroxide for 6 hours at 100°C under a pressure of 0.5 to 1.0 mm Hg, a sample of the bis - oxide was prepared which showed a strong absorption in the infra-red spectrum at 785 cm^{-1}, attributable to the Sn—O—Sn linkage. No absorption characteristic of the Sn—OH linkage was evident, indicating that the compound had been entirely dehydrated to the bis - oxide.

H. Tricyclopentyltin Phenoxide

The phenoxide was prepared by heating to the boiling point a solution containing 17.15 g tricyclopentyltin hydroxide, 4.71 g phenol and 200 cc benzene. The by-product water (10.8 cc) was removed during the reaction. Evaporation of the solvent yielded 21.05 g of a yellow oil, $\eta_D^{26}=1.5627$.

Analysis:	Found:	Sn, 28.04%; —OC_6H_5 residue, 24.0%
	Calculated:	Sn, 28.32%; —OC_6H_5 residue, 22.2%

I. Tricyclopentyltin Chloride (From the Hydroxide)

To a suspension of 17.15 g tricyclopentyltin hydroxide in 100 cc of pentane was added 6 cc of a 36% aqueous hydrochloric acid solution with stirring. The organic phase was separated and dried over magnesium sulphate after adding 3 g sodium sulphate and 100 cc ether to break up the emulsion. After filtering, the pentane phase was stripped of solvent to yield 17.05 g of white crystals, melting from 39.5 to 42.5°C.

Analysis:	Found:	Sn, 32.60%; Cl, 9.82%
	Calculated:	Sn, 32.83%; Cl, 9.81%

Analysis by vapor phase chromatography indicated that the product was over 95% pure.

J. Tricyclopentyltin Dimethyldithiocarbamate

To a solution containing sodium dimethyldithiocarbamate dihydrate (5.38 g) and 50 cc water was added a solution of 10.84 g tricyclopentyltin chloride in 50 cc acetone. The mixture was stirred for 1 hour and then poured into a separatory funnel.The lower phase was added to 100 cc of acetone. The aqueous phase was extracted once with 50 cc hexane, the hexane added to the acetone solution and the mixture dried using anhydrous magnesium sulphate for 1-1/2 hours. After filtering, the solvent was removed under reduced pressure to yield 13.15 g of a beige solid, that melted from 55 to 57°C.

Analysis:	Found:	Sn, 26.67%; S total 14.48%
	Calculated:	Sn, 26.60%; S total 14.30%

K. Tricyclopentyltin 4-acetylaminobenzoate

A mixture of 17.15 g tricyclopentyltin hydroxide, 9.0 g 4 - acetylaminobenzoic acid and 250 cc benzene were heated to the boiling point using a Dean-Stark trap to isolate the water formed. 0.8 cc of water was collected over a 1.5 hour period. The hot solution was filtered and allowed to cool to room temperature as crystals were deposited. The crystals were filtered and dried under vacuum. Yield=21.49 g of white crystals melting from 169 to 174°C.

Analysis:	Found:	Sn, 23.87%; Acid No. 113
	Calculated:	Sn, 23.54% Acid No. 111

L. Tricyclopentyltin 2-aminonicotinate

A mixture of 17.2 g tricyclopentyltin hydroxide, 6.90 g 2 - aminonicotinic acid and 250 cc benzene was heated to the boiling point using a Dean-Stark trap to collect the water (0.9 cc) formed as a by-product The hot solution was filtered and allowed to cool to room temperature, during which time it deposited 22.26 g of yellow solids melting from 92 to 98°C. The crude product was recrystallized from 250 cc heptane to yield 11.48 g of white crystals melting from 101 to 103°C. When evaporated to 1/2 of the original volume under reduced pressure and cooled to 0°C the heptane solution deposited another 7.5 g of white crystals melting from 99 to 101°C. Both crops were combined and analyzed.

Analysis:	Found:	Sn, 26.29%; Acid No. 123
	Calculated:	Sn, 25.63%; Acid No. 121

M. Bis[tricyclopentyltin] Sulphide

To an aqueous solution containing 12.1 g of disodium ethylenebis(dithiocarbamate) in 150 cc water was added dropwise over 1/4 hour a solution of 25 g tricyclopentyltin chloride and 150 cc acetone. Solids initially formed, but during 1 hour of stirring the solid changed to a yellow oil suspended in a viscous liquid. The mixture was poured into a separatory funnel and 75 cc of ether were added. The aqueous phase was removed and the organic phase added to 100 cc acetone. The organic phase was dried over anhydrous magnesium sulphate. Evaporation of the solvent yielded 31.19 g of a mixture of yellow viscous liquid and solids. 200 cc of benzene were added and the mixture was heated. The crude product was then cooled to 25°C and filtered. The filtrate was stripped of solvent to give 24.25 g of a yellow liquid plus solids. This mixture was filtered and over a period of four days the filtrate partially solidified. The resultant mixture was recrystallized from 100 cc isopropanol to yield 6.6 g of yellow crystals melting from 70 to 72°C.

Analysis:

Found:	Sn, 34.87;	S total 4.39%
Calculated for $[(C_5H_9)_3Sn]_2S$:	Sn, 34.70;	S total 4.69%

N. Tricyclopentyltin 2-thiophene Carboxylate

18.8 g of tricyclopentyltin hydroxide and 6.4 g 2 - thiophene carboxylic acid were heated to the boiling point for 2 hours in 200 cc benzene, during which time 0.6 cc water collected in the Dean-Stark trap. The hot reaction mixture was filtered, then freed of solvent under reduced pressure to yield 24.54 g of a white solid melting from 58 to 62°C.

Analysis:	Found:	Sn, 26.43%;	Acid No. 118
	Calculated:	Sn, 26.20%;	Acid No. 124

O. Bis[tricyclopentyltin] Adipate

The adipic acid derivative was prepared in a manner similar to the foregoing procedure N using 18.8 g tricyclopentyltin hydroxide and 3.65 g adipic acid. 0.85 cc of water was collected during the reaction. On removing the benzene, 20.63 g of a white solid were isolated and melted from 61 to 65°C. Recrystallization from 100 cc methanol yielded 18.55 g of white crystals that melted from 66 to 69°C.

Analysis:	Found:	Sn, 29.46%;	Acid No. 142
	Calculated:	Sn, 29.81%;	Acid No. 141

P. Tricyclopentyltin Thiophenoxide

A mixture of 18.8 g tricyclopentyltin hydroxide, 5.5 g thiophenol and 200 cc benzene was heated to the boiling point. 0.84 cc of water was collected over a 1.5 hour period. The resultant solution was filtered and solvent evaporated to yield 22.9 g of yellow liquid product, $\eta_D^{24}=1.5885$.

Analysis:	Found:	Sn, 29.25;	S, 6.68%
	Calculated:	Sn, 25.29;	S, 6.82%

Q. Tricyclopentyltin 1,2,4-triazole

A mixture of 18.8 g tricyclopentyltin hydroxide, 3.45 g 1,2,4 - triazole and 200 cc toluene was heated to the boiling point for 1 hour during which time 0.82 cc of water was collected using a Dean-Stark trap. 100 cc of toluene was then distilled off and the hot solution was filtered. On cooling, crystals were deposited which, when isolated and dried, weighed 19.1 g. One recrystallization from boiling toluene yielded 17.9 g of product melting from 204.5 to 210°C.

Analysis:	Found:	Sn, 30.16;	N, 11.37%
	Calculated:	Sn, 30.12;	N, 10.66%

EXAMPLE 2

Preparation of Tri - (2 - cyclopentylethyl)tin Bromide and Derivatives Thereof

A. Tetra(2-cyclopentylethyl)tin

To a solution containing 0.5 mole of cyclopentylethyl magnesium bromide prepared in the conventional manner from 0.5 mole 2 - cyclopentyl - 1 - bromoethane, 0.5 g atom magnesium chips and 250 cc tetrahydrofuran was added a

solution containing 26.0 g (0.1 mole) stannic chloride and 100 cc benzene. The addition was gradual and required 0.5 hour to complete, after which the reaction mixture was heated to the boiling point for 2 hours and then allowed to cool to ambient temperature. The product was then hydrolyzed using a solution of 15 g of citric acid in 250 cc of water. The organic portion of the resultant two-phase liquid was isolated and the water therein removed using anhydrous magnesium sulphate. The solvent was evaporated under reduced pressure to yield 59.3 g of a semi-solid material which was combined with 100 cc of isopropanol and stirred for one hour. The resultant slurry was filtered, washed with cold (0°C) methanol and dried to yield 49.15 g of a white solid that melted from 74 to 77°C.

Analysis:	Found:	Sn, 22.41%; Cl, 0.13%
	Calculated:	Sn, 23.40%; Cl, 0.0%

B. Cleavage of Tetra(2-cyclopentylethyl)tin to Tri(cyclopentyl)tin Bromide

To a solution containing 40.6 g tetra(2 - cyclopentylethyl)tin, 90 cc chloroform and 35 cc methanol maintained at 0°C was added dropwise over 5 hours a solution of 12.8 g bromine in a mixture of 50 cc methanol and 50 cc chloroform. When the addition was complete, the mixture was allowed to warm to 25°C and the solvents were then evaporated under reduced pressure to yield 41.7 g of white solids. These were recrystallized from 150 cc methanol by cooling to –20°C. The crystals were filtered, washed with methanol at a temperature of –60°C and dried under reduced pressure. The first crop of crystals weighed 24.4 g and melted from 55 to 58°C. The mother liquor solution was evaporated to 1/3 of the original volume then cooled to 0°C whereupon it deposited a second crop of crystals which were filtered and dried. This crop weighed 7.9 g and melted from 58 to 60°. The two crops when combined weighed 32.3 g.

Analysis:

	Found:	Sn, 23.90%; Br, 15.22%
Calculated for tri(cyclopentylethyl)tin bromide:		Sn, 24.22%; Br, 16.31%

C. Bis[tri(cyclopentylethyl)tin] Oxide

To a solution containing 1.6 g (0.04 mole) of sodium hydroxide, 50 cc methanol and 50 cc water was added a solution containing 9.8 g tri(cyclopentylethyl)tin bromide, 100 cc methanol and 40 cc acetone. The addition was gradual and required 10 minutes. Following completion of the addition the reaction mixture was heated to the boiling point (67°C) for two hours, then cooled to ambient temperature, after which 150 cc of water and 100 cc of diethyl ether were added and the resultant mixture was stirred vigorously for five minutes. The organic phase of the resultant two-phase liquid was isolated and freed of water using anhydrous magnesium sulphate. The drying agent was removed after two hours and the solvent was evaporated under reduced pressure to yield 8.2 g of a yellow oil which was found to contain 27.33% tin. The tin content of pure bis[tri(cyclopentylethyl)tin] oxide is 28.38. Analysis by vapor phase chromatography demonstrated that the compound was 91.4% pure.

EXAMPLE 3

Preparation of Tri(2-cyclopentylmethyl)tin Bromide

Tetra(cyclopentylmethyl)tin was prepared using the procedure described in Example 2 from cyclopentylmethylmagnesium bromide and stannic chloride. The product was a solid melting from 63 to 66°C and contained 27.86% tin. The calculated tin content of tetra(cyclopentylmethyl)tin is 26.30%.

Tetra(cyclopentylmethyl)tin was cleaved by reacting the compound with bromine using the procedure described in the preceding Example. Following one recrystallization from methanol the product melted from 32 to 34°C and was found to contain 26.34% tin and 17.84% bromine. The calculated values for tri(cyclopentylmethyl)tin bromide are 26.49% for tin and 17.84% for bromine.

EXAMPLE 4

Preparation of Tri(cyclopentylmethyl)tin Chloride and the Corresponding Oxide

Methyltri(cyclopentylmethyl)tin was prepared by reacting 0.425 mole of cyclopentylmethylmagnesium bromide with 30.5 g methyltin trichloride in 150 cc of benzene. The crude product was isolated from the reaction mixture as a yellow

oil (48.3 g) of refractive index 1.5192 at 24° and in 85% purity. After washing twice with methanol (75 cc and 25 cc) and distillation under reduced pressure, 33.8 g of product boiling at 140°C under 0.3 mm Hg were obtained, η_D^{24}=1.5230. Vapor phase chromatography showed the material to be 95.6% pure.

To a solution of methyltri(cyclopentylmethyl)tin (26.8 g) in 100 cc of pentane, was added dropwise a solution of stannic chloride (18.2 g) in 100 cc pentane over 20 minutes. The resultant yellow solution was heated to the boiling point for 0.5 hour then cooled to room temperature. The mixture was combined with a solution containing 2 cc 12N hydrochloric acid and 98 cc water, following which the organic phase was separated and washed with a mixture of 2 cc 12N hydrochloric acid and 98 cc water. The organic phase was again separated and the water therein removed using anhydrous magnesium sulphate. After filtration, the solvent was removed under reduced pressure to yield 28.20 g of a white solid that melted from 88 to 90°C.

Analysis:

Found:	Sn, 29.21;	Cl, 8.87%
Calculated for tri(cyclopentylmethyl)tin chloride:	Sn, 29.41;	Cl, 8.80%

Vapor phase chromatography indicated the compound to be 98.3% pure.

Bis[tri(cyclopentylmethyl)tin] Oxide

To a solution containing 1.8 g sodium hydroxide, 10 cc water and 10 cc methanol was added dropwise a solution containing 12.11 g tris(cyclopentylmethyl)tin chloride and 25 cc tetrahydrofuran over 15 minutes. An oil formed initially and dissolved as the addition proceeded. When the addition was complete, the solution was stirred at 25°C for 0.5 hour. 300 cc of cold (10°C) water was added followed gy 200 cc of diethyl ether with vigorous stirring. The organic phase was isolated and the water therein removed using anhydrous magnesium sulphate. After filtration the solvent was removed under reduced pressure to yield 11.28 g of a waxy solid melting from 59 to 63°. The crude product was purified by adding 60 cc methanol and cooling to 0°C whereupon a small amount of solid material precipitated. The solid was removed and the filtrate evaporated under reduced pressure to yield 11.35 g of yellow liquid, η_D^{25}=1.5296.

Analysis:

Found:	Sn, 30.16
Calculated for bis[tri(cyclopentylmethyl)tin] oxide:	Sn, 31.56

Assay by potentiometric titration=92.6% purity.

EXAMPLE 5

Preparation of Tri(2 - methylcyclopentyl)tin Chloride and the Corresponding Oxide

A. Methyltri(2-methylcyclopentyl)tin

To a solution containing 0.31 mole of 2 - methylcyclopentylmagnesium bromide in 150 cc of tetrahydrofuran was added a solution containing 21.6 g methyltin trichloride in 150 cc dry toluene over a period of 1 hour. When the addition was complete, the mixture was heated to the boiling point for 2 hours and then stirred at 25°C for 16 hours. The reaction mixture was then hydrolyzed using a solution containing 25 g citric acid and 250 cc water. The organic phase was separated and the water therein removed using anhydrous magnesium sulphate. The liquid phase was then evaporated under reduced pressure to yield 25.45 g of crude product. Low boiling impurities were distilled off at from 25 to 75°C under a pressure of 0.1 mm Hg. The residue, which contained the desired product, weighed 33.85 g and exhibited a refractive index of 1.5192 at 24°C.

Analysis:

Found:	Sn, 30.11
Calculated for methyl tri(2-methylcyclopentyl)tin:	Sn, 30.98

B. Tri(2-methylcyclopentyl)tin Chloride

To a solution containing 13.4 g of methyl tri(2 - methylcyclopentyl)tin and 50 cc of hexane was added over a 0.5 hour period a solution containing 9.1 g of stannic chloride and 50 cc of hexane. Following completion of the addition the resultant

mixture was heated to the boiling point for 15 minutes then cooled to 25°C. The reaction mixture was then hydrolyzed by addition of a solution containing 2 cc concentrated (12N) hydrochloric acid and 100 cc of water. The organic phase of the resultant two-phase liquid was isolated and combined with a second portion of the aforementioned hydrochloric acid solution. The organic phase was again isolated and the water therein removed using anhydrous magnesium sulphate. The liquid phase was then evaporated under reduced pressure to yield 14 g of a yellow oil that exhibited a refractive index (η_D^{21}) of 1.5333 and was found to contain 28.48% tin and 8.61% chlorine. The calculated values for the desired chloride are 29.4% tin and 8.78% chlorine.

C. Bis[tri(2-methylcyclopentyl)tin] Oxide

Bis[tri(2 - methylcyclopentyl)tin] oxide was prepared by gradually adding a solution containing 8.1 g of the corresponding chloride (prepared as described in the foregoing paragraph) 25 cc methanol and 15 cc acetone to a solution containing 1.2 g of sodium hydroxide, 20 cc water and 50 cc methanol. The addition required 0.5 hour, following which the resultant solution was heated to the boiling point for 10 minutes, and then cooled to 15°C, while 300 cc of water were gradually added. The resultant mixture was stirred for 1 hour while the temperature was maintained at 15°C. 50 cc of diethyl ether was then added while the mixture was stirred at high speed. The organic phase of the resultant two-phase liquid was isolated and the water therein removed using anhydrous magnesium sulphate. The liquid was then evaporated under reduced pressure to yield 7.6 g of a pale yellow oil which was found to contain 30.54% tin. The calculated tin content of bis[tri(2 - methylcyclopentyl)tin] oxide is 31.56%. A potentiometric titration of the product indicated that it was 98% pure.

Biological Activity of Tricyclopentyltin and Tri(cyclopentylalkyl)tin Compounds

The following procedures were employed to evaluate the efficacy of the triorganotin compounds according to the invention in controlling a number of representative fungi and insects.

Procedure 1—Employed Using Two-spotted Spider Mite (Tetranychus urticae), Beet Army Worm (Spodoptera exigua) and Cabbage Looper (Trichoplusia ni)

A cotton plant with two fully expanded leaves is dipped into an aqueous dispersion of the test compound. An additional portion is injected into the soil at the root zone. Lepidopterous insect larvae are dipped into the water dispersion and placed in petri dish cages clamped around the treated foliage. When using the two-spotted spider mite as the test insect the dipping step is not performed since the mites are on the leaf before the plant is treated. A mortality count is taken six days after treatment.

Procedure 2—Employed Using Tobacco Black Shank Fungus (Phytophthora parasitica var. nicotiane)

Tobacco plants are transplanted into soil infested with the test organism. Immediately after transplanting the soil is drenched with a solution of test chemical. The test is graded on the basis of plant survival.

Procedure 3—Employed Using Bean Mildew (Erysiphe polygoni)

Bean seeds are planted in fumigated soil which is then drenched with a solution of the test compound. When the plants reach a suitable size they are inoculated with the fungus. After 7 days the relative number of healthy plants is noted.

Procedure 4—Employed Using Grape Downy Mildew (Plasmopara viticola) Rice Blast (Pericularia oryzae and Apple Powdery Mildew (Podosphaera leucotricha)

Host plants, (grape, rice or apple, depending upon the fungus) are sprayed with a water suspension of the test compound and then inoculated with the pathogen. After disease symptoms are well developed on untreated control plants the test plants are graded for disease control.

Procedure 5—Secondary Evaluation of Activity In Combatting Two-spotted Spider Mite (Tetranychus bimaculatis) and Aphid

Bean plants infested with the organism are sprayed with a water dispersion

containing the test compound. The percent mortality is observed three days after spraying.

Procedure 6—Employed Using Codling Moth Larvae (Carpocapra ponomella)

Codling moth eggs are placed on a paraffin surface that has previously been treated with a water dispersion of the test compound. The paraffin is perforated, allowing the newly hatched larva to feed on an underlay of food. After six days a mortality count is made.

Procedure 7—Employed Using Bollworm Larvae

Five third instar bollworm larvae are placed in pepri plates containing a layer of semi-synthetic diet. These larvae are sprayed with 3 cc of a 400 ppm solution or suspension of the chemical from a distance of 15 inches using a Spraying Systems Company nozzle 40100-120. After spraying, the petri dish cover is replaced with a fiber brewer lid to permit limited air exchange. Following a holding period of up to 3 days, mortality counts are made.

Procedure 8—Employed Using Apple Scab (Venturia inaequalis)

Apple seedlings are infected with the fungus. The seedlings are then sprayed with an aqueous solution or suspension of the test chemical. After a period of incubation the plants are rated for disease control.

Procedure 9—Employed Using Hornfly Larvae

The test compound is mixed with calf feces and hornfly eggs are introduced. After 2 days observation is made to determine the presence of fly larvae.

Procedure 10—Employed Using Cabbage Looper (Trichoplusia ni) To Determine Sustems Activity

A water dispersion of the test compound is injected into the root zone of a bean plant that is infested with the cabbage looper. Mortality counts are made 3 to 6 days after treatment.

Procedure 11—Employed Using Cabbage Looper (Trichoplusia ni)

A bean plant is sprayed with a water dispersion of test compound and a number of cabbage loopers are placed on the treated foliage. A check for mortality is made after 3 days.

Procedure 12—Employed Using Cabbage Looper To Determine Ovicical Activity

The test chemical is dissolved in a suitable water-miscible solvent and diluted with water to the desired concentration. Eggs of the cabbage looper, having been deposited by the adult insects on paper toweling or other substrate, are fastened to the underside of a test plant leaf with methocel or other appropriate adhesive. Egg sheets are selected having 25—50 eggs per plant. Cotton or other appropriate host plants are used. The leaf of the plant to which eggs are attached is dipped in the solution containing the test chemical. Ovicidal observations are recorded 3—5 days after treatment. Inactive materials show large areas of foliage consumed by freshly emerged larvae.

Procedure 13—Employed Using Western Spotted Cucumber Beetle Larvae

Seventy-five grams of air-dried soil are placed in 236 cc capacity round bottle and treated with sufficient volume of a solution containing 400 ppm of the chemical to give 25 ppm of toxicant on an air-dried soil basis. The treated soil after being allowed to air dry is mixed by shaking and rolling.

Eggs of the western spotted cucumber beetle (laid over a period of 3 or 4 days) are collected and a measured quantity of eggs are suspended in water. The egg concentration is 70—80 eggs/0.5 cc of solution. A portion of the suspension containing about 50 eggs is pipetted into the bottom of a clear plastic medicinal via. An amount of treated soil sufficient to cover the eggs is added, a corn seed is placed on the soil and covered with additional treated soil.

The soil, eggs and seed mix is watered and additional water is added as necessary to maintain growth of the seedling corn plant. Care must be taken not to add too much water or the larvae will drown. After a period of from 6—9 days an observation is made to determine the presence of larvae both on top of the soil and at the roots of the seedling.

Procedure 14—Employed Using Codling Moth Larvae To Determine Ovicidal Activity and Control of Newly Hatched Larvae

The test chemical is dissolved in a small amount of a suitable water-miscible solvent and diluted with water to achieve the desired concentration. The chemical solution is applied to apples or pears which are then covered with eggs of the codling moth. The fruit is then incubated for from eight to ten days in a greenhouse. The number of living and dead larvae are then counted and compared with a sample of untreated fruit used as a control.

Procedure 15—Employed Using Mosquito Larvae

Third or early fourth instar larvae of *Aedes aegypti* are used for the test organism. Twenty to twenty-five larvae are placed in distilled water containing the candidate chemical. Activity is recorded as the concentraion (ppm) constituting a lethal dose for 95 percent of the population (LD_{95}).

Procedure 16—Employed Using Apple Powdery Mildew

Aqueous solutions or suspension of the experimental chemical are poured into cups of vermiculite in which plants are growing. The aqueous system usually contains acetone and a wetting agent, both in non-toxic amounts. Two to four days after the compound is applied the leaves are wet with a spore suspension of apple powdery mildew. The plants are then put int a greenhouse. When disease symptoms are clear, the plants are graded. Untreated plants are rated as "0% control" and the disease free plants are rated as 100% control.

The accompanying tables summarize the data obtained using the aforementioned procedures with representative compounds encompassed by the accompanying claims.

TABLE I

Biological Activity of Tricyclopentyltin Hydroxide Against Fungi

Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Tobacco Black Shank	2	25	100
	2	6.3	100
Bean Mildew	3	25	100
Grape Downy Mildew	4	100	100
	4	6.2	95
Rice Blast	4	100	93
	4	25	67
Apple Powdery Mildew	4	100	100
	4	25	95

TABLE II

Biological Activity of Tricyclopentyltin Hydroxide Against Insects

Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Spider Mite	5	400	100
	5	100	100
	5	25	86
Beet Army Worm	1	400	100
Cabbage Looper	1	100	100
Codling Moth Larvae	6	400	100
Bollworm Larvae	7	400	100
Aphid	5	400	100

TABLE III

Biological Activity of Tricyclopentyltin Chloride as a Fungicide

Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Apple Scab	8	100	90
Rice Blast	4	400	95
	4	100	70
Apple Powdery Mildew	16	100	70

TABLE IV

Biological Activity of Tricyclopentyltin Chloride as an Insecticide

Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Cabbage Looper	1	400	100
Codling Moth Larvae	14	400	100

TABLE V

Biological Activity of Tricyclopentyltin Acetate as a Fungicide

Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Grape Downy Mildew	4	400	100
		100	90
Apple Powdery Mildew	4	100	90

TABLE VI

Biological Activity of Tricyclopentyltin Acetate as an Insecticide

Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Cabbage Looper	12	400	90
		100	90
Cucumber Beetle Larvae	13	25	100

TABLE VII

Biological Activity of Tricyclopentyltin Fluoride as an Insecticide and Fungicide

Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Spider Mite	1	400	99
		100	97
Cabbage Looper	1	400	100
Codling Moth Larvae	14	400	100
Grape Downy Mildew	4	400	100
		100	94
		50	80
Rice Blast	4	400	96
		100	80
Apple Powdery Mildew	4	100	90

TABLE VIII

Biological Activity of Tricyclopentyltin Bromide

Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Spider Mite	1	400	100
Cabbage Looper	1	400	100
		25	83
Mosquito Larvae	15	1	100
Tobacco Black Shank	2	25	100
Grape Downy Mildew	4	400	97
		100	100
Apple Powdery Mildew	4	400	90
		100	97
		6.3	75

TABLE IX

Biological Activity of Tri(cyclopentylethyl)tin Hydroxide

Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Spider Mite	5	400	95
		100	98
		25	50
Grape Downy Mildew	4	400	100
		100	85
		25	50
Apple Scab	8	400	100

TABLE X

Biological Activity of Tri(cyclopentylethyl)tin Bromide

Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Cabbage Looper	1	400	83
Hornfly Larva	9	100	100
Tobacco Black Shank	2	25	100
Apple Powdery Mildew	4	400	75

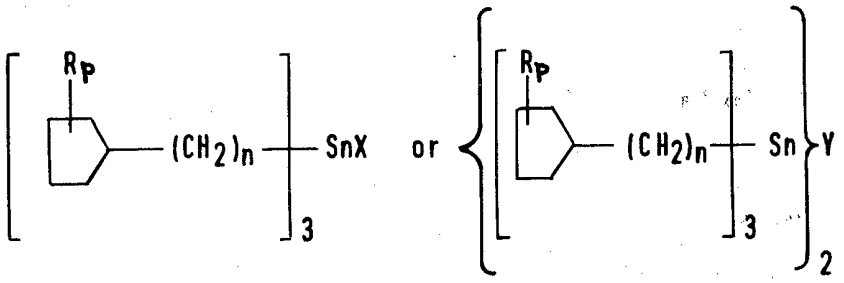
TABLE XI

Biological Activity of Tri(2-methylcyclopentyl)tin Chloride

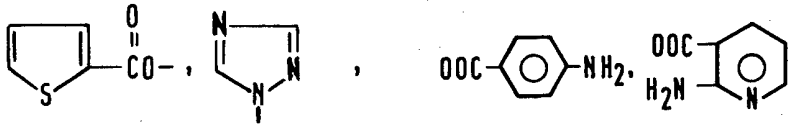
Organism	Proc. No.	Concentration (ppm)	Control Rating (%)
Cabbage Looper	1	400	100
Grape Downy Mildew	4	400	100
Apple Scab	8	400	100
		100	60

WHAT WE CLAIM IS:—

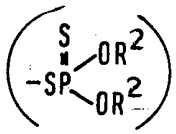
1. A triorganotin compound of formula



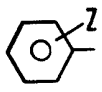
wherein R is an alkyl group containing from 1 to 3 carbon atoms, n is 0, 1 or 2 and p is 0 or 1, with the proviso that at least one of n and p is always 0, and that when n and p are both 0, X represents fluorine, nitrate, cyanate, thiocyanate, carbamoyloxy, thiocarbamoyloxy carboxylate (—OOCR^1) other than acetoxy, dithiocarbamoyl, alkoxy (OR^1), phenoxy, thiophenoxy, mercaptide, (—SR^1),



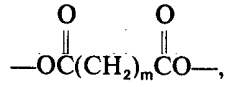
or



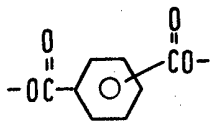
R^1 being an alkyl group containing from 1 to 12 carbon atoms and R^2 being an alkyl group containing from 1 to 12 carbon atoms or a phenyl group,



wherein Z is hydrogen, halogen, an alkyl or alkoxy group containing from 1 to 3 carbon atoms or nitro and Y is



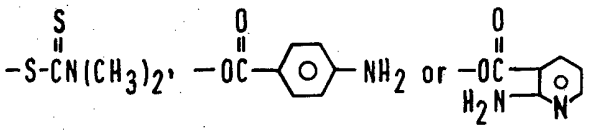
m being an integer from 2 to 10, inclusive,



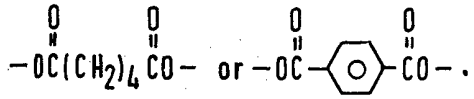
sulphur, sulphate or carbonate; with the proviso that when either n or p is not 0, X also represents hydroxyl or acetoxy and Y also represents oxygen.

2. A triorganotin compound according to Claim 1, wherein Y is oxygen.

3. A triorganotin compound according to Claim 1, wherein X is



4. A triorganotin compound according to Claim 1, wherein Y is sulphur,



5. A composition for killing fungi and insects, which consists essentially of an inert liquid or solid carrier and a fungicidally and insecticidally effective amount of a triorganotin compound as claimed in any one of the preceding claims or of tricyclopentyltin hydroxide, chloride, bromide or acetate.

6. A compound according to Claim 1, when prepared substantially as described in any one of the foregoing Examples, other than Examples 1(B), 1(D), 1(I) and 3.

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