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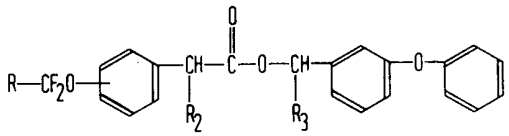
(72) Inventors GERALD BERKELHAMMER and VENKATARAMAN KAMESWARAN

(54) *m*-PHENOXYBENZYL ESTERS OF ARALKANOIC ACIDS AND THEIR USE AS INSECTICIDAL AND ACARICIDAL AGENTS

(71) We, AMERICAN CYANAMID COMPANY, a company organised and existing under the laws of the State of Maine, United States of America, of Berdan Avenue, Township of Wayne, State of New Jersey, United States of America, 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:—

This invention relates to novel m-phenoxybenzyl esters of aralkanoic acids which show activity as insecticidal and acaracidal agents.

The compounds of the present invention may be represented by formula (I):

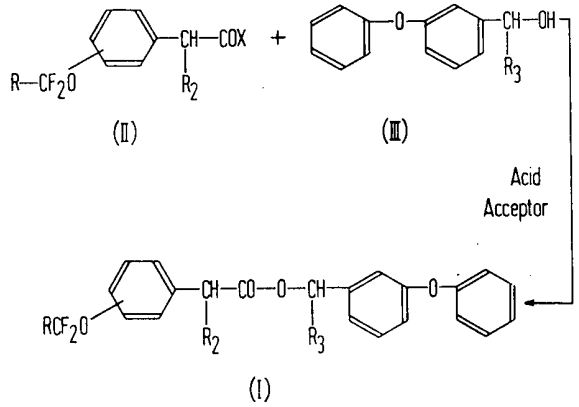


(1)

wherein RCF_2O— is *m* or *p* to the carbon to which the alkanoic acid esters group is attached and wherein *R* represents H, F, Cl, CHF_2 or CF_3; R_2 represents ethyl, *n*-propyl, isopropyl, isopropenyl or *t*-butyl and R_3 is hydrogen or cyano; and including the optical isomers thereof.

The present invention also provides a method for controlling insects and acarina by contacting the insects and acarina, their habitat, breeding grounds and/or their food supply, with an insecticidally or acaricidally effective amount of a compound of formula (I). The invention thus includes a method for protecting agronomic crops, either growing ar harvested, from attack by insects and/or acarina. The invention further includes a method for the systemic control of insects and acarina that feed on the body fluids of livestock and domestic animals, comprising orally or parenterally administering to the animal host a systemically effective amount of a formula (I) compound.

Advantageously, the novel *m*-phenoxybenzyl esters of a 2-(haloalkylphenyl)-alkanoic acid, depicted by formula (I), can be prepared by reacting an alpha substituted (haloalkoxyphenyl)acetyl halide, (II), preferably chloride, with a *m*-phenoxybenzyl alcohol (III). The reaction is generally conducted in the presence of a solvent such as diethyl ether, benzene, or toluene, at a temperature between about 10°C and 30°C in the presence of an acid acceptor. Among the acid acceptors that can be employed are the tertiary organic amines, trimethylamine, triethylamine and pyridine. This reaction can be illustrated as follows:



wherein RCF_2O is *m* or *p* to the carbon to which the alkanoic acid group is attached and wherein R is H, F, Cl, CHF_2 or CF_3; R_2 is ethyl, *n*-propyl, isopropyl, *t*-butyl or isopropyl; R_3 is H or CN and X is halogen, preferably chlorine.

The preferred compounds within the generic formula I depicted above, can be categorized as (1) those wherein RCF_2O— is *p*- to the carbon to which the alkanoic acid acid ester group is attached and R, R_2 and R_3 are as defined above; or (2) those wherein RCF_2O— is *m*- to the carbon to which the alkanoic acid ester group is attached to R, R_2 and R_3 are as defined above.

Within each of these groups we have found that compounds where R is F, R_3 is CN and R_2 is ethyl, *n*-propyl, isopropyl, *t*-butyl or isopropenyl are preferred.

With regard to the compounds of the present invention as depicted by formula I, it should also be understood that various optical isomers of the above-identified compounds do result from the preparations described.

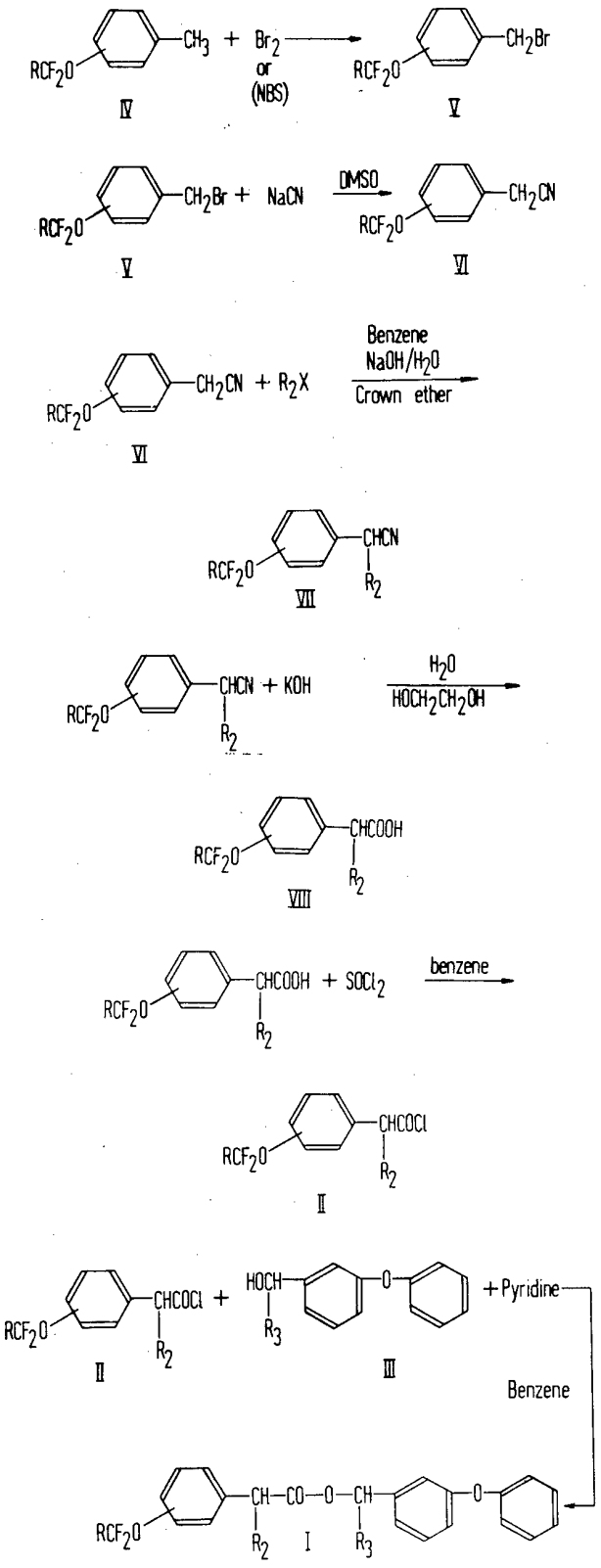
For example, in the synthesis of formula I esters, wherein R_3 is hydrogen, a chiral center is present at R_2 and *d* and *l* isomeric pairs are formed. Also, α-cyano substitution at R_3 introduces an additional chiral center thus allowing for an additional *d*, *l* pair. All such optical isomers are included within the scope of the present invention.

The α-substituted (haloalkoxyphenyl)acetyl halide II, can be prepared using the appropriate haloalkoxyl toluene IV as a starting material. The process for the preparation involves five steps, the first of which is the halogenation of the haloalkoxytoluene IV with, for example, bromine, chlorine or N-bromosuccinimide (NBS). This reaction is preferably conducted in the presence of an inert organic solvent such as carbon tetrachloride, and a radical initiator such as light, benzoyl peroxide, or azo-*bis*-isobutyronitrile, to yield the haloalkoxybenzylahide V. The formula V haloalkoxybenzylhalide is then converted to the corresponding haloalkoxyphenylacetonitrile VI by reaction with sodium or potassium cyanide in the presence of a solvent, suitably dimethylsulfoxide (DMSO) or ethanol at an elevated temperature. This (haloalkoxyphenyl)acetonitrile VI is then readily alkylated when treated with an alkyl halide in the presence of base and an inert organic solvent; crown ethers have been found to be useful catalysts in this reaction. The α-alkyl(haloalkoxyphenyl)acetonitrile formed in the above reaction is depicted by formula VII and hydrolysis of this formula VII α-alkyl(haloalkoxyphenyl)acetonitrile, using an alkali metal hydroxide in the presence of an alkylene glycol and water, yields the α-alkyl(haloalkoxyphenyl) acetic acid shown as formula VIII. Treatment of the formula VIII acid with e.g. thionyl chloride or thionyl bromide, preferably in the presence of an aromatic solvent such as benzene or toluene, then yields the α-substituted (haloalkoxyphenyl) acetyl halide II which is reacted with the *m*-phenoxybenzyl alcohol II or α-cyano-*m*-phenoxybenzyl alcohol to yield the desired *m*-phenoxybenzyl ester or a α-cyano-*m*-phenoxybenzyl ester of the 2-(haloalkoxyphenyl)-alkanoic acid I.

These reactions are graphically illustrated in Flow Diagram I below.

Flow Diagram I

Preparation of *m*-phenoxybenzyl esters of 2-(haloalkoxyphenyl)alkanoic acid



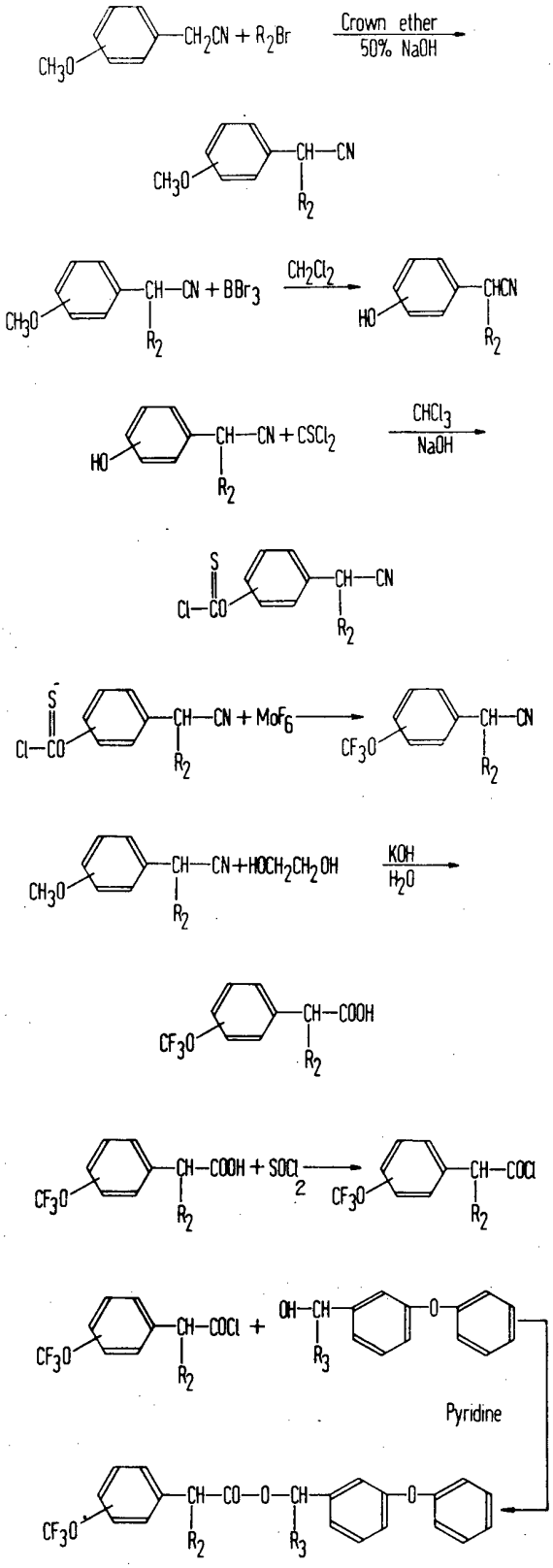
Preparation of the *m*-phenoxybenzyl and α-cyano-*m*-phenoxybenzyl esters of α-alkyl-3 (or 4)-trifluoromethoxyphenyl)acetic acid can also be accomplished by a sequence beginning with the alkylation of *m*- or *p*-methoxyphenylacetonitrile, using an alkyl halide in the presence of a crown ether and base. It is of course obvious that when the *m*-methoxyphenylacetonitrile is used in this reaction the α-alkyl-3-methoxyphenyl acetonitrile is obtained and when the *p*-isomer is employed the α-alkyl-4-methoxyphenylacetonitrile is obtained. It will likewise become apparent from the following discussion that the location of the methoxy group on this phenylacetonitrile starting material determines the position of the trifluoromethoxy substituent in the final product.

The α-alkyl-3(4)-methoxyphenylacetonitrile, referred to above, is converted to the α-alkyl-3(4)-hydroxyphenylacetonitrile by treatment with boron tribromide, preferably in the presence of a solvent such as methylene chloride. Treatment of the thus-formed alcohol with thiophosgene and base in the presence of a solvent such as chloroform, then yields the chlorothio ester of O-[*m* or *p*-(1-cyano-2-methylpropyl)-phenyl]formic acid. This ester is readily converted to the α-alkyl-3(4)trifluoromethoxyphenylacetonitrile with molybdenum hexafluoride and this compound is then hydrolyzed to the corresponding α-alkyl-3(4)-trifluoromethoxyphenyl acetic acid by reaction with ethylene glycol in the presence of an alkali metal hydroxide and water.

Treatment of the α-alkyl-3(4)-trifluoromethoxyphenyl acetic acid with thionyl chloride in the presence of an aromatic solvent such as benzene or toluene, yields the corresponding acid chloride which reacts with *m*-phenoxybenzyl alocohol or α-cyano-*m*-phenoxybenzyl alcohol to give the desired *m*-phenoxybenzyl or α-cyano-*m*-phenoxybenzyl α-alkyl-3(or 4)-trifluoromethoxyphenylacetate.

These reactions are graphically illustrated in Flow Diagram 2 below.

Flow Diagram 2.



In the reactions set forth in Flow Diagram 2, R_2 is ethyl, *n*-propyl, isopropyl or *t*-butyl and R_3 is hydrogen or cyano.

With respect to the formation of the α-cyano-*m*-phenoxybenzyl ester products by the procedures illustrated in either Flow Diagram I or II, it is not necessary to prepare the α-cyano-*m*-phenoxybenzyl alcohol precursor. It is equally or more satisfactory to allow a mixture of *m*-phenoxybenzaldehyde, an alkali cyanide such as sodium cyanide, and the appropriate α-substituted (haloalkoxyphenyl)acetyl halide to react together in one step to form the final α-cyano ester.

The reader's attention is directed to our co-pending Application No. 24866/78 divided herefrom which is directed to α-alkyl(haloalkoxyphenyl) acetic acids, (and to processes for their preparation), which are intermediates in the above-described processes of this invention.

The compounds of the invention are active as contact and stomach poisons for ixodide ticks and for a wide variety of insects, particularly Dipterous, Lepidopterous, Coleopterous and Homopterous insects. Preferred compounds of this invention are unusual among pyrethroids, in that they exhibit a very extended residual insectidal activity on plant tissue, as compared with known pyrethroids such as permethrin, phenothrin and allethrin, they are effective in the soil, and are surprisingly effective for the control of ixodidae and the protection of animals against attack by insects and ixodidae when administered to the animals orally or parenterally or applied thereto as a topical insecticidal or acaricidal formulation. They do not require admixture with a stabilizing agent to achieve insecticidal and acaricidal compositions havng stabilized effects; however, they may be used in combination with other biological chemicals, for example pyrethroid synergists such as piperonyl butoxide, sesamex or *n*-octyl sulfoxide of isosafrole. They may also be used in combination with conventional insecticides such as the phosphates, carbamates, formamidines, chlorinated hydrocarbons or halobenzoylureas. To achieve control of insects, including soil insects which attack growing plants and/or harvested crops, including stored grain, the insecticidal compounds of this invention may be applied to the foliage of plants, the insect's habitat and/or the insect's food supply. Generally, the active compound is applied in the form of a dilute liquid spray; however, it may also be applied as an aerosol, a dust, a granular, or a wettable powder formulation. The present compounds are particularly effective for the control of tobacco budworm.

Liquid sprays which are particularly useful are oil sprays and emulsifiable concentrates which can be further diluted for application. While they are, respectively, prepared as liquid concentrates; for convenience in handling and shipping, these formulations are usually dispersed in water at the site of their use and then applied as a dilute spray to the plant foliage, soil or surface of the area being treated.

A typical emulsifiable concentration useful for protecting a variety of crops such as cereals, cole crops, curbits, corn, cotton, tobacco, soybeans, ornamentals and shrubs, may comprise about 20% by weight of the active agent; 4% by weight of an emulsifying agent, conventionally employed in the preparation of pyrethroid formulations; 4% by weight of a surfactant; 25% by weight of an organic solvent such as cyclohexanone; and about 47% by weight of a petroleum solvent having a minimum aromatic content of about 83 volume %.

For use as animal systemic insecticidal and acaricidal agents, the compounds of this invention can be administered to the animal host either orally or parenterally. When given orally, it may be in any convenient form designed for oral administration such as a bolus, capsule, tablet or as an oral drench. The active agent may also be incorporated in an edible animal feedstuff such as a nutritionally balanced diet containing from 0.0001% to 0.1% and preferably 0.001 to 0.05% by weight of feed of the active compound.

If desired, the systemic insecticidal and acaricidal agent may be introduced into the body of the animal by subcutaneous, intramuscular or intraperitoneal injection, such that it may be distributed through the animal's body by the action of the animal's circulatory system. In practice, the systemic agent may be dissolved or dispersed in a pharmaceutically acceptable carrier such as water, propylene glycol, vegetable oil, or glycerol formal for administration.

Advantageously, the systemic agents have a good margin of safety and are effective for protecting a variety of animals, particularly livestock and laboratory and domestic animals such as cattle, sheep, horses, dogs and cats, from attack by such pests as fleas, mosquitoes, flies and ticks. The present compounds for the control of mosquitoes.

Among the compounds of this invention which are useful as insecticidal and acaricidal agents are:

m-Phenoxybenzyl α-isopropyl-4-trifluoromethoxyphenylacetate.
β-Cyano-*m*-phenoxybenzyl α-isopropyl-4-trifluoromethoxyphenylacetate.
α-Cyano-*m*-phenoxybenzyl α-isopropyl-3-trifluoromethoxybenzylacetate.
α-Cyano-*m*-phenoxybutyl α-ispropoyl-4-chlorodifluoromethoxyphenylacetate.
m-Phenoxybenzyl α-isopropyl-4-(1,1,2,2-tetrafluoromethoxy)-phenylacetate.
α-Cyano-*m*-phenoxybenzyl α-isopropyl-4-pentafluoroethoxyphenylacetate.
m-Phenoxybenzyl α-ethyl-3-trifluoromethoxyphenylacetate.
α-Cyano-*m*-phenoxybenzyl α-*n*-propyl-4-chlorodifluoromethoxyphenylacetate.
α-Cyano-*m*-phenoxybenzyl α-t-butyl-4-trifluoromethoxyphenylacetate.

The invention is illustrated by the examples set forth below. Examples 1—6 and 9—14 relate to the preparation of intermediates.

Example 1.

Preparation of *p*-1,1,2,2-tetrafluoroethoxy)toluene.

For 1 hour tetrafluoroethylene and nitrogen are bubbled into a magnetically stirred mixture of 10.8 g (0.100 moles) of *p*-cresol, 1.67 g (1.43 g real, 0.0255 moles) of potassium hydroxide pellets, and 70 ml of dried dimethylformamide (DMF) maintained at 68°C. After dilution with 250 ml of water, the reaction mixture is extracted with 100 ml of ether. The ether solution is washed with 200 ml of 5% sodium hydroxide and twice with 400 ml of water. The ether solution is dried, filtered, and then rotary evaporated to give 18.14 g (87%) of *p*-(1,1,2,2-tetrafluoroethoxy)toluene.

Analysis calculated for $C_9H_8F_4O$:
C, 51.93%; H, 3.87%; F, 36.15%.
Found:
C, 52.06%; H, 3.76%; F, 41.52%.

Example 2.

Preparation of *p*-(1,1,2,2-tetrafluoroethoxy)benzyl bromide.

A mechanically stirred mixture of 118.45 g (0.569 moles) of *p*-1,1,2,2-tetrafluoroethoxy)toluenee, 123.00 g, 0.691 moles, 121 mole%) of N-bromosuccinimide (NBS), 1.00 g (4.13 moles, 0.73 mole%) of benzoyl peroxide, and 350 ml of carbon tetrachloride is refluxed for 2.25 hours. After cooling, the reaction mixture is diluted with 350 ml of carbon tetracloride, filtered to remove the solids, dried with sodium sulfate, filtered, and then evaporated, using a rotary evaporator, to give 160.99 g (99%) of a clear red oil. This product is used as is in the subsequent reactions. Infrared and NMR show the product to be *p*-(1,1,2,2-tetrafluoroethoxy)benzyl bromide.

Example 3.

Preparation of *p*-(1,1,2,2-tetrafluoroethoxy)phenylacetonitrile.

Over a period of 40 minutes a hot solution of 75.1 g (1.15 moles) of potassium cyanide in 140 ml of water is added to a mechanically stirred 75°C solution of 160.99 g (0.561 moles) of *p*-(1,1,2,2-tetrafluoroethoxy)benzyl bromide and 500 ml of anhydrous 2B alcohol. The resulting mixture is refluxed for 1.75 hours. After sitting overnight the reaction mixture is poured into 500 ml of cold water and 400 ml of ether. The combined ether solutions are washed twice with 500 ml of water, dried with sodium sulfate, filtered, and then evaporated on a rotary evaporator to give 114.95 g of an oil. A vacuum distillation of this oil gives, as one distillation fraction, 37.10 g (28%) of the nitrile, boiling point 85°C to 100°C at 0.29 mm Hg.

Example 4.

Preparation of α-isopropyl-p-(1,1,2,2-tetrafluoroethoxy)phenylacetonitrile.

A mixture of 39.85 g (0.171 moles) of *p*-1,1,2,2-tetrafluoroethoxy)phenylacetonitrile, 3.71 g (9.96 mmoles, 5.8 mole%) of dicyclohexyl-18-crown-6, 22.0 ml (28.8 g, 0.234 moles) of 2-bromopropane, 55 ml of benzene, and 55 ml of 50% sodium hydroxide is stirred for 45 minutes during which there is an exotherm from 25°C to 43°C. The reaction mixture is then heated at 45°C for 16.5 hours. After dilution with 200 ml of water the reaction mixture is extracted with 200 ml of ether. The ether solution is washed with 400 ml of 12% hydrochloric acid, 200 ml of 5%

hydrochloric acid, and 300 ml of water. The ether solution is dried with sodium sulfate, filtered, and then evaporated to give 47.13 g of an oil. This oil is vacuum distilled to give 34.83 g (74%), boiling point 83°C to 85°C at .055—.090 mm Hg.

Analysis calculated for $C_{13}H_{13}F_4NO$:
C, 56.73%; H, 4.76%; N, 5.09%; F, 27.61%.
Found:
C, 56.12%; H, 4.85%; N, 4.99%; F, 34.07%.

Example 5.

Preparation of 3-methyl-2-[*p*-1,1,2,2-tetrafluoroethoxy)-phenyl]-butyric acid.

A stirred mixture of 48.0 g (24.0 g real, 0.60 moles) of 50% sodium hydroxide, 21.78 g (0.0791 moles) of α-isopropyl-p-(1,1,2,2-tetrafluoroethoxy)phenylacetonitrile,and 240 ml of ethylene glycol is heated at 135°C for 12 hours. After dilution with 600 ml of water the reaction mixture is washed twice with 100 ml of ether. The water layer is acidified with concentrated hydrochloric acid and then extracted twice with 300 ml of ether. The ether solution is washed twice with 500 ml of water, dried with sodium sulfate, filtered, and then evaporated to give 20.74 g (89%) of a brown solid, melting point 92°C to 97°C (hexane).

Analysis calculated for $C_{13}H_{14}F_4O_3$:
C, 53.06%; H, 4.80%; F, 25.83%.
Found:
C, 53.04%; H, 4.79%; F, 25.93%:

Example 6.

Preparation of 3-methyl-2-[*p*-1,1,2,2)-tetrafluoroethoxy)-phenyl]butyryl chloride.

A stirred mixture of 20.00 g (0.0680 moles) of 3-methyl-2-(*p*-(1,1,2,2-tetrafluoroethoxy)phenyl]butyric acid, 20.00 ml (33.2 g, 0.280 moles) of thionyl chloride (Baker), and 75 ml of dried benzene is refluxed for 4 hours. The reaction mixture is then evaporated and the resulting residue is diluted with 50 ml of benzene and again evaporated to give 22.46 g (106%) of a clear dark brown liquid. This product is used as is in the subsequent reactions. The liquid is examined by infrared analysis and determined to be the above-named product.

Example 7.

Preparation of *m*-phenoxybenzyl α-isopropyl-4-(1,1,2,2-tetrafluoroethoxy)-phenylacetate.

To a stirred mixture of 6.81 g (0.0340 moles) of *m*-phenoxybenzyl alcohol, 3.0 ml (2.95 g, 0.0372 moles) of dried pyridine, and 20 ml of methylene chloride is added over a period of 20 minutes a 20 ml methylene chloride solution of 10.6 g (0.034 moles) of 3-methyl-2-[*p*-1,1,2,2-tetrafluoroethoxy)phenyl]butryl chloride. The reaction mixture is stirred at room temperature for 66 hours and then diluted with 200 ml of ether. The ether solution is washed with 200 ml of 20% hydrochloric acid and 200 ml of water, dried with sodium sulfate, filtered, and then evaporated to give 16.24 g (100%). This product is purified on a silica gel dry column (116 cm × 5 cm, eluent = 1:1 hexane-methylene chloride) by collecting a sample between 85 cm and 63 cm (solvent front = 113 cm) to give 12.60 g (78%) of a clear silghtly yellow colored oil.

Analysis calculated for $C_{26}H_{24}F_4O_4$:
C, 65.54%; H, 5.08%; F, 15.95%.
Found:
C, 64.99%; H, 4.96%; F, 19.10%.

Example 8.

Preparation of α-cyano-m-phenoxybenzyl, α-isopropyl-4-(1,1,2,2-tetrafluoroethoxy)-phenylacetate.

To a stirred mixture of 8.81 g (7.49 g real, 0.0333 moles) of α-cyano-*m*-phenoxybenzyl alcohol, 3.0 ml (2.95 g, 0.0372 moles) of dried pyridine, and 20 ml of methylene chloride was added, over aperiod of 20 minutes, a 20-ml methylene chloride solution of 10.6 g (0.034 moles) of 3-methyl-2-[*p*-(1,1,2,2-tetrafluoroethoxy)phenyl]butyryl chloride. The reaction mixture is stirred at room temperature for 66 hours and then diluted with 200 ml of ether, washed with 200 ml of 20%

hydrochloric acid and 200 ml of water, dried with sodium sulfate, filtered, and then evaporated to give a dark red oil. In order to remove the *m*-phenoxybenzaldehyde impurity the oil is reacted with 0.5 g of sodium borohydride at ice bath temperatures and the resulting oil is purified on a silica gel dry column (121 cm × 5 cm, eluent = 1:1 hexane-methylene chloride) by collecting a sample between 77 cm and 57 cm (solvent front = 113 cm) to give 11.17 g (66%) of a clear orange oil.

Analysis calculated for $C_{27}H_{23}F_4NO_4$:
C, 64.67%; H, 4.62%; N, 2.79%; F, 15.16%.
Found:
C, 65.26%; H, 4.81%; N, 2.82%; F, 17.94%.

Example 9.

Preparation of α-isopropyl-4-methoxyphenylacetonitrile.

A solution of sodium hydroxide (50%, 300 ml) is added to a solution of *p*-methoxyphenylacetonitrile (147 g, 1 mole), dicyclohexyl-18-crown-6 (18.63 g, 5 mole percent), 2-bromopropane (320 g, 2.6 mole) and benzene (300 ml). The reaction mixture is heated to 45°C and held for 4 days. The organic phase is separated, washed well with water (3 × 200 ml), dilute hydrochloric acid (1 × 200 ml) and evaporated to an oil. Vacuum distillation gives the product (175.6 g, 81% real): boiling point 96°C to 100°C (0.15 mm); nmr ($CDCl_3$) shows that the distilled material contains 12.5 mole percent of the starting nitrile.

Example 10.

Preparation of α-isopropyl-4-hydroxyphenylacetonitrile.

Boron tribromide (51.0 g, 0.2 mole) in methylene chloride (20 ml) is added to a solution of α-isopropyl-4-methoxyphenylacetonitrile (37.8 g, 0.2 mole) in methylene chloride (35 ml) maintained at −40°C. The red solution is allowed to wram to room temperature and stirred for 3 days. The reaction solution is added to ice, then extracted with ether (3 × 100 ml), washed with water (2 × 100 ml) and evaporated to an oil. Vacuum distillation gives the product: α-isopropyl-4-hydroxyphenylacetonitrile (28.9 g, 81%); boiling point 142°C to 143°C (0.25 mm).

Example 11.

Preparation of formic acid, chlorothio, O-[*p*-(1-cyano-2-methylpropyl)phenyl]ester.

Thiophosgene (16.43 g, 0.143 mole) in chloroform (50 ml) is added over 30 minutes to a solution of α-isopropyl-4-hydroxyphenylacetonitrile (25.0 g, 0.143 mole) in NaOH solution (5%, 5.72 g, 0.143 mole), using an ice bath occasionally to maintain the temperature below 30°C. The mixture is stirred for 15 minutes and the chloroform layer is separated, washed with water and evaporated to a yellow oil (38.2 g). The product is used as such in Example 12.

Example 12.

Preparation of α-isopropyl-4-trifluoromethoxyphenylacetonitrile.

The thiocarbonate (38.2 g) from Example 12 is treated with molybdenum hexafluoride (15.8 g) at −25°C. The thick reaction mass is then allowed to warm to room temperature and then heated slowly to 160°C using an oil bath. The mixture is cooled to room temperature and then poured into water and extracted with ether (4 × 50 ml), washed with water (1 × 50 ml) and evaporated to an oil. Vacuum distillation gives α-ispropyl-4-trifluoromethoxyphenylacetonitrile; boiling point 78°C to 80°C (0.15 mm).

Example 13.

Preparation of α-isopropyl-4-trifluoromethoxyphenylacetatic acid.

A mixture of α-isopropyl-4-trifluoromethoxyphenylacetonitrile (2.0 g), potassium hydroxide (3.0 g) in ethylene glycol (35 ml) and water (3 ml) is heated at 140°C for 8 hours. The solution is poured into water and extracted with ether (2 × 10 ml). The aqueous layer is acidified with dilute hydrochloric acid and extracted with ether (3 × 11 ml), washed with water (1 × 25 ml), dried (Na_2SO_4) and evaporated to an oil (1.23 g); IR (neat) 1700 cm^{-1}.

Example 14.

Preparation of α-isopropyl-4-trifluoromethoxyphenylacetyl chloride.

A solution of α-isopropyl-4-trifluoromethoxyphenylacetic acid (1.2 g) and thionyl

chloride (0.6 ml) in benzene (5 ml) is refluxed for 4 hours. Evaporation of the solvent and excess thionyl chloride gives the acid chloride which is used as such for esterification in Examples 15 and 16.

Example 15.

Preparation of α-cyano-*m*-phenoxybenzyl α-isopropyl-4-trifluoromethoxyphenylacetate.

A solution of α-isopropyl-4-trifluoromethoxyphenylacetic chloride (4.58 mmole) in either (5 ml) is added to a ether (20 ml) solution of α-cyano-*m*-phenoxybenzyl alcohol (4.58 mmole) and pyridine (0.5 ml). The mixture is stirred overnight and filtered. The filtrate and the washings are evaporated and the residual oil is purified on 5 × 2 mm silica gel plates using 1:1 methylenechloride-hexane as eluent. The band with Rf=0.55 is extracted with ether and evaporated to give the desired ester (0.85 g).

IR (neat) 1755 cm^{-1}; NMR ($CDCl_3$) δ 6.8—7.6 (m, 13H, Ar*H*), 6.31 and 6.28

(S, 1H, —CH(CN)—Ar),

3.27 (d, J=7Hz, 1H, C*H*—$CH(CH_3)_2$), 2.0—2.6 (m, 1H, C*H*$(CH_3)_2$), 0.6—1.2 four doublets, J=7Hz, 6H, isopropyl CH_3); ^{19}F chemical shift 58.8 δ relative to $CFCl_3$.

Example 16.

Preparation of *m*-phenoxybenzyl α-isopropyl-4-trifluoromethoxyphenylacetate.

The above ester is prepared from *m*-phenoxybenzyl alcohol and α-isopropyl-4-trifluoromethoxyphenylacetyl chloride using the same procedure as described in Example 14.

IR (neat) 1738 cm^{-1}; NMR ($CDCl_3$) w 6.73—7.45 (m, 13H), 5.03 (S 2H), 3.20 (d, J=10.5 Hz, 1H), 2.26 (m, 1H), 0.66 and 0.94 (two d, J=6.6 Hz, 6H).

Example 17.

Insecticidal Activity.

The insecticidal activity of compounds of this invention is demonstrated in the following tests, wherein Tobacco budworm, *Heliothis virescens* (Fabricus); Western Potato Leafhopper, *Empoasca abrupta* DeLong and Bean Aphid, Aphis fabae (Scopoli), are employed as test insect species. Procedures employed are as follows:

Tobacco Budworm *Heliothis virescens* (Fabricius).

First Instar.

A cotton plant with two true leaves expanded is dipped for 3 seconds with agitation in a test solution (35% water/65% acetone) containing 300, 100 or 10 ppm of test compounds. Each leaf is placed in a cup with a wick and a piece of cheesecloth infested with 50—100 newly hatched larvae is added before covering the cup with a lid. After 3 days at 80°F, 50% r.h., the cups are examined and the kill of newly hatched larvae noted. Data obtained are reported as percent kill in Table I.

Bean Aphid, *Aphis fabae* (Scopoli).

Five cm fiber pots, each containing a nasturtium plant 2 inches high and infested with 100 to 150 aphids 2 days earlier are placed on a 4 rpm turntable and sprayed with a 35% water/65% acetone solution containing 100, 10, 1.0 and 0.1 ppm of test compound for 2 revolutions using a DeVilbis Atomizer ("DeVilbis" is a registered Trade Mark) and 20 psi air pressure. The spray tip is held about 15 cm from the plants and the spray directed so as to give complete coverage of the aphids and the plants. The sprayed plants are laid on their sides on white enamel trays. Mortality estimates are made after 1 day at 70°F., 50% r.h.

Data are reported as percent mortality determined at the rate indicated (Table I).

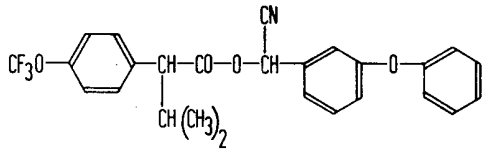
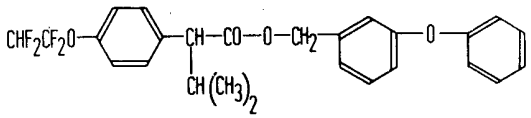
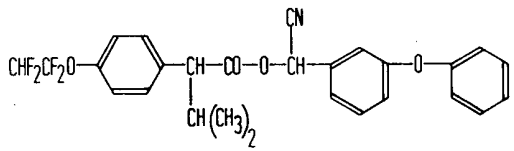
Western Potato Leafhopper, *Empoasca abrupta* DeLong.

A Sieve lima bean plant with the primary leaf expanded to 3 to 4 inches is dipped into a 35% water/65% acetone solution containing 100, 10 or 1 ppm of test compound. The dipped plant is placed in the hood to dry and then a 2.5 cm piece of the tip of one leaf is cut off and placed in a 4-inch petri dish with a moist filter paper in the bottom. From 3 to 10 second-instar nymphs are placed in the

dish and the dish is then covered. Mortality counts are made after holding the thus-prepared dishes for 2 days at 80°F and 50% r.h. Data obtained are reported in Table I.

TABLE I

INSECTICIDAL EVALUATION

Compound	% Mortality									
	Tobacco Budworm Larvae 1st Instar			Leaf Hopper			Aphids			
	ppm			ppm			ppm			
	300,	100,	10	100,	10,	11	100,	10,	1,	.1
	100	100	100	100	100	70	100	100	90	50
	90	90	0	50	0	–	100	100	0	–
	100	100	0	100	0	–	100	100	50	–

Example 18.

The insecticidal activity of compounds of the present invention is further demonstrated by the following tests.

The procedures employed for evaluation against mosquito larvae, Mexican Bean Beetles and Southern Armyworks are as follows.

Malaria Mosquito—Anapheles quadrimaculatus Say.

1 Milliliter of a 35% water/65% acetone solution containing 300 ppm of test compound is pipetted in a 400 ml beaker containing 250 ml of deionized water and stirred with the pipette, giving a concentration of 1.2 ppm. Aliquots of this solution are taken and further diluted to .4, .04, and .004 ppm. A wax paper ring 0.6 cm wide to fit inside the beaker is floated on the surface of the test solution to keep the eggs from floating up the meniscus curve and drying out on the side of the glass. A spoon made of screen is used to scoop up and transfer about 100 eggs (0—24 hours old) into the test beaker. After 2 days at 80°F., 50% r.h., observations of hatching are made. Percent mortality records are presented in Table II.

Mexican Bean Beetle—Epilachna varivestis Mulsant.

Sieve lima bean plants (2 per pot) with primary leaves 7.5 to 10 cm long, are dipped in the 300, 100, 10 or 1 ppm test solution and set in the hood to dry. One leaf is removed from the plant and placed in a 10 cm petri dish containing a moist filter paper on the bottom and 10 last-instar larvae (13 days from hatching). The day after treatment, another leaf is removed from the plant and fed to the larvae after removing the remains of the original leaf. Two days after treatment, the third leaf is fed to the larvae, this usually being the last needed. The fourth leaf is used on the third day after treatment if the larvae have not finished feeding. The test is now set aside and held until adults have emerged, usually in about 9 days after treatment began. After emergence is complete, each dish is examined for dead larvae, pupae or adults; deformed pupae or adults; larvae-pupal intermediates or pupal-adult intermediates; or any other interference with normal molting, transformation and emergence of pupae or adults.

Data obtained are reported in Table II.

Southern Armyworm—*Spodoptera eridania* (Cramer).

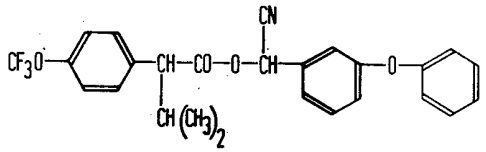
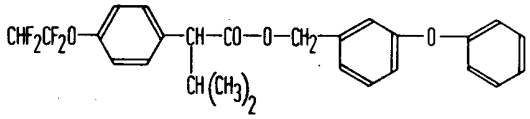
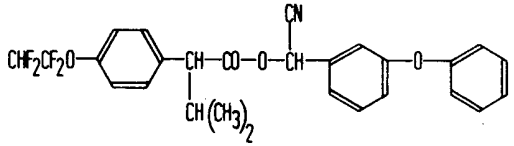
Methods:

Sieva lima bean plants, with two expanded 7.5 to 10 cm primary leaves, are dipped three seconds with agitation in the treatment solutions and then set in a hood to dry. After the leaves are dry they are excised and each excised leaf is placed in a 10 cm petri dish containing a piece of moist filter paper and 10 third-instar southern armyworm larvae approximately 1 cm long. The petri dishes are covered and placed in a holding room for 2 days at a temperature of 80°F and 50% relative humidity.

Mortality counts are made after 2 days. Results obtained are presented in Table II.

TABLE II

INSECTICIDAL EVALUATION

Compound	% Mortality										
	Mosquito Larvae				Southern Armyworm			Mexican Bean Beetle			
	ppm				ppm			ppm			
	1.2	0.4	.04	.004	1000	100	10	300	100	10	1
	100	100	100	90	100	100	100	100	100	100	100
	100	100	90	0	100	100	0	100	–	–	–
	100	100	80	0	100	100	0	100	–	–	–

– = Not Tested

Example 19.

Insecticidal Activity.

Two-Spotted Spider Mite—*Tetranychus urticae* (Koch).

Sieva lima bean plants, with primary leaves three 7.5 to 10 cm long, are infested with about 100 adult phosphate resistant mites per leaf four hours before use in this test, in order to allow egg-laying before treatment. The infested plants are dipped for three seconds with agitation into the 1000, 300, 100 or 10 ppm solution, and the plants set in the hood to dry. After 2 days at 80°F., the adult mite mortality is estimated on one leaf under a 10X stereoscopic microscope. The other leaf is left on the plant an additinoial five days and then examined at 10X power to estimate the kill of eggs and of newly-hatched nymphs, giving a measure of ovicidal and residual action, respectively. Test results are provided in Table III.

Tobacco Budworm—*Heliothis virescens* (Fabricus) Third Instar.

Three cotton plants with just expanded cotyledons are dipped in 1000 or 100 ppm solution and placed in the hood to dry. When dry, each cotyledon is cut in half, and 10 leaf sections are each placed in a 28 g plastic medicine cup containing a 1.25 cm dental wick saturated with water and one third-instar budworm larva is added. The cup is capped and held for 3 days at 80°F 50% r.h., after which mortality counts are made. Test results are provided in Table III.

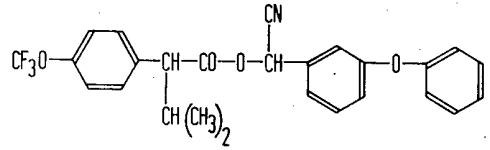
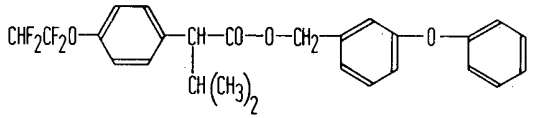
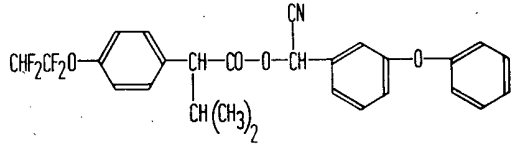
Cabbage Looper—*Trichoplusia ni* (Hübner)—Third Instar.

A true leaf on a cotton plant is dipped into the test solution containing 1000, 100 or 10 ppm of test compound, agitated for 3 seconds, and removed to dry in an exhaust hood. When dry, the leaf is placed in a 9.0 cm petri dish with moist filter paper on the bottom. Ten third-instar larvae are added and the lid placed on the dish Mortality counts are made after 3 days at 80°F and 50 ± 10% r.h.

Data obtained are reported in Table III below.

TABLE III

INSECTICIDAL ACTIVITY

Compound	% Mortality								
	Phosphate Resistant mites				3rd Instar Tobacco Budworm		3rd Instar Cabbage Looper		
	ppm				ppm		ppm		
	1000	300	100	10	1000	100	1000	100	10
	100	100	80	0	100	100	100	100	100
	–	100	50	0	50	1	100	0	–
	–	90	60	0	80	0	100	30	0

– ≡ Not Tested.

Example 20.

Soil Insecticidal Activity.

Southern Corn Rootworm—Diabrotica undecimpunctata howardi Barber.

Ten mg of compound are diluted to 10 ml with acetone to make a stock solution (A). Two ml of this solution is then diluted to 10 ml with acetone to make solution B. Approximately 0.7 g Pyrax ABB talc is then placed in a 28 g widemouth jar and 1.25 ml of the selected solution is added to the talc to produce the following concentrations:

1.25 ml solutions A yields 56 kg/ha.

1.25 ml solution B yields 11.2 kg/ha.

The selected test solution is mixed with the talc to wet it evenly before it is dried under an air-jet dryer for 10—15 minutes. Twenty-five ml of moist sterilized potting soil and approximately 0.6 g millet seed (food for larvae) and then added to the jars containing test compound. The jars are capped and the contents mixed on a vibrating mixer. Each jar then receives 10 Southern Corn Rootworm larvae which are 6—8 days old. The jars are loosely capped and placed in a holding room at 80°F and 50% r.h. with constant light. Mortality counts are made after 6 days.

In this test α-cyano-*m*-phenoxybenzyl, α-isopropyl-4-trifluoromethoxyphenyl-acetate gave 100% control of Southern Corn Rootworms at the 56 kg/ha rate and 70% control at the 11.2 kg/ha rate.

Example 21.

Residual insecticidal activity obtained with foliar treatment of cotton plants.

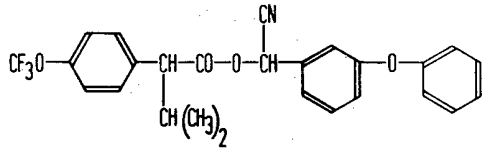
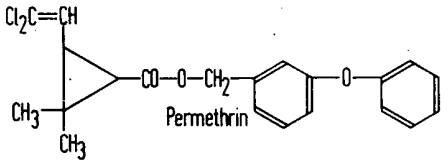
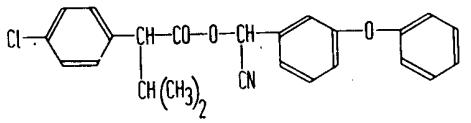
Young cotton plants with at least two expanded true leaves growing in 10 cm plastic pots were dipped, usually one leaf at a time, in a 65% acetone—35% water solution of test compound with agitation for three seconds. The concentration of each compound in the solutions was 30 ppm, 100 ppm, 300 ppm or 900 ppm of active ingredient.

After the leaves had dried, two leaves from each of two plants were excised and placed in petri dishes (90 mm × 10 mm) on moist filter paper. Five third instar tobacco budworm larvae were placed on each leaf and the petri dish capped. The infested dishes were then placed in the holding room with continuous light, ambient temperature of 80°F and 50% r.h. Larval counts were made after 72 hours.

The remaining plants were placed under high intensity lights in the greenhouse adjusted to provide 14 hours of light per day. Leaf samples were assayed with third instar tobacco budworm larvae after 3, 7, 10 and 14 days exposure in the greenhouse.

TABLE IV

Residual Insecticidal Activity of Test Compounds on Cotton Plants Using Third-Instar Tobacco Budworm Larvae for Bioassay

Compound	Rate ppm	Days Residual Activity									
		0		3		7		10		14	
		1*	2**	1	2	1	2	1	2	1	2
	30	90	0	90	0	60	0	60	0.03	60	1.3
	100	100	0	100	0	100	0	95	0	95	.03
	300	100	0	100	0	100	0	100	0	100	0
	900	100	0	100	0	100	0	100	0	100	0
	30	65	0.3	30	11.3	15	12.5	40	4.3	5	57.5
	100	85	0	85	.03	70	.53	65	0.6	25	1.0
	300	100	0	100	0	100	0	65	0	80	0
	900	100	0	100	0	100	0	90	0	100	0
 South Africa 73/4462	30	65	.03	65	.1	75	.05	45	2.3	75	.03
	100	100	0	85	0	100	0	90	0.03	100	0
	300	95	0	100	0	100	0	95	0	95	0
	900	100	0	100	0	100	0	100	0	100	0
Check	–	0	100	0	96.3	5	90	0	73.8	13	80

*1 = Average % Mortality 20 TBW/Point **2 = Average % Feeding Damage.

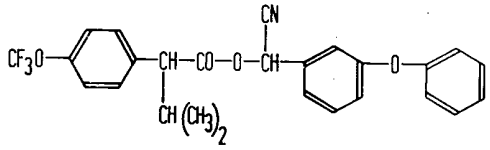
Example 22.

Ixodicidal Activity.

Eeffective control of acarina larvae is demonstrated in the following tests with larvae of *Boophilus microplus*, a one-host tick which can remain on a single host thrcugh its three lift stages, i.e., larvae, nymph and adult. In these tests, a 10% acetone—90% water mixture contains .025, .1, .5, 2.5 or 12.5 ppm of test compound. Twenty larvae are enclosed in a pipet sealed at one end with a gauze material and solution containing the test compound is then drawn through the pipet with a vacuum hose, thereby simulating a spray system. The ticks are then held for 48 hours at room temperature and mortality is determined. The results achieved are set forth below.

TABLE V

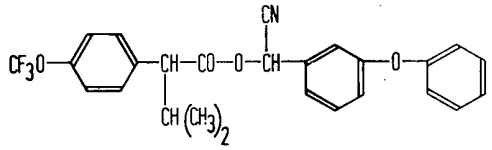
Percent Larval Tick Mortality of *Boophilus microplus* Larvae

Compound PPM	12.5	2.5	0.5	0.1	0.025
	100	100	100	100	100

The above procedure is repeated excepting that the concentration of test compound is 0.1, 0.025, 0.005 or 0.001.

TABLE VI

Percent Mortality of *Boophilus microplus* Larvae

Compound PPM	0.1	0.025	0.005	0.001
	100	100	80	80

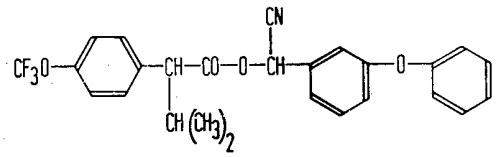
Example 23.

The effectiveness of compounds of the invention for controlling adult *Boophilus microplus* ticks is determined in the following tests wherein test compound is made up in solutions as described in Example 22, excepting that sufficient compound is used to give solutions containing 125, 52.6, 31.2, 15.6 or 7.3 ppm of test compound.

Adult engorged female ticks are then dipped in the test solutions for 3 seconds and placed in individual containers and held for 48 hours in a room maintained at 80°F and 50% r.h. At the end of the holding period the ticks are examined and egg deposits counted. Engorged females that do not deposit eggs are considered dead. Data obtained as reported below in Table VII.

TABLE VII

Ixodicidal Activity Against Adult *Boophilus microplus*

Compound	Percent Adult Tick Mortality at Concentrations (ppm)				
	125	62.5	31.2	15.6	7.3
	100	100	99.4	98.8	87.2

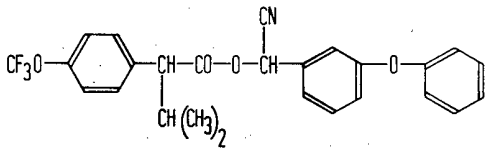
Example 24.

The effectiveness of the compounds of the invention for controlling Screwworms *Cochliomyia hominivorax,* a very destructive livestock pest, is demonstrated in the following test wherein first instar larvae of *Cochliomyia hominivorax* are permitted to feed on a mixture of ground beef (8.0 g), blood (7.0 ml), H_2O (2.1 ml) and formulation (0.9 ml) containing 1, 5 or 25 ppm of test compound.

Two replicates of 20 larvae per dosage level are used in the evaluations. Larvae are permitted to feed *ad libitum* for 24 hours on the composition medium. After this period the number of dead larvae for each treatment and each replicate are determined and percent mortality calculated. Data obtained are reported in Table VIII below.

TABLE VIII

Evaluation of Compounds for the Control of Screwworm Larvae *Cochiomyia hominivorax*

Compound	Percent Mortality at Concentration (PPM)		
	1	5	25
	2.4	69.2	100

Example 25.

Determinations of LC_{50} for test compounds against Tobacco Budworm on cotton plants.

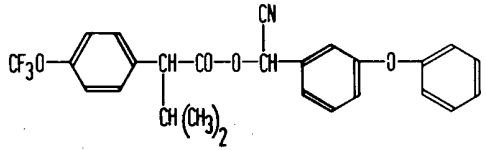
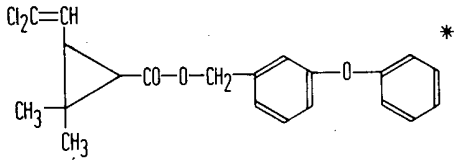
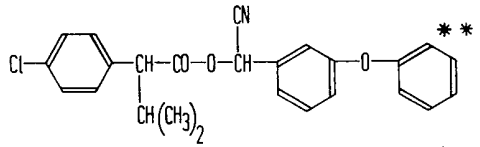
Young cotton plants with at least two expanded true leaves growing in 10 cm plastic pots were dipped, usually one leaf at a time, in a 65% acetone—35% water solution of test compound with agitation for three seconds. The concentration of each compound in the solutions was 1.1 ppm, 2.8 ppm, 7.5 ppm, 20 ppm, 60 ppm or 150 ppm of active ingredient.

After the leaves had dried, two leaves from each of two plants were excised and placed in petri dishes (90 mm × 10 mm) on moist filter paper. Five third instar tobacco budworm larvae were placed on each leaf and the petri dish capped. The

infested dishes were then placed in a holding room with continuous light ambient, temperature of 80°F and 50% r.h. Larval counts were made after 72 hours. Each treatment was replicated 4 times. Data obtained are reported in Table IX below where it can be seen that the compound of the subject invention is about 2 to 5 times more effective for the control of tobacco budworms than were the art compounds evaluated in the same test.

TABLE IX

Determination of LC_{50} for Test Compounds Against Third-Instar Tobacco Budworms

Compound	Dose (ppm)	No. Insects in Test	No. Insects Dead	LC_{50}
	1.10 2.80 7.50 20.00 60.00	20 20 20 20 20	3 9 18 19 20	2.94
 *	7.50 20.00 60.00 150.00	20 20 20 20	2 16 19 20	14.6
 **	2.80 7.50 20.00 60.00 150.00	20 20 20 20 20	3 13 17 20 20	6.4

* = Permethrin **= Disclosed South African Patent Application 73/4462.

Example 26.

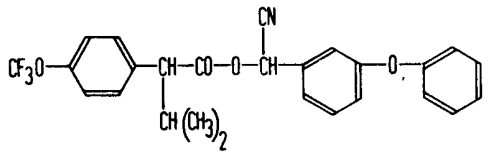
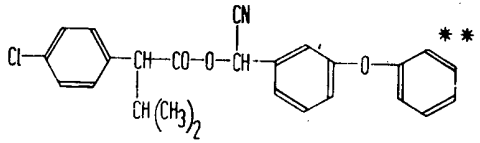
Determination of LC_{50} for test compounds against adult mosquitoes *Anopheles quadrimaculatus Say.*

The compounds to be evaluated were prepared in acetone at the desired concentration in ppm. To produce an aerosol application the insecticide solutions were pipetted (0.15 ml) into the top of a nozzle and siphoned through the atomizer nozzle. The atomized droplets are carried by an air stream (4 miles/hour) to the caged mosquitoes (25 adult females/cage) for a 4—5 second exposure. The mosquitoes were then anesthetized (3—4 seconds) with CO_2 and transferred to holding cages. The holding cages of treated mosquitoes were placed in a holding room at 85 ± 1°F and 46 ± 2% relative humidity Mortality counts were made after 24 hours.

Data obtained are reported in Table X below where it can be seen that the compound of the invention was approximately four times more effective than the art compound for controlling adult *Anopheles quadrimaculatus.*

TABLE X

LC_{50} Determinations of Test Compounds Against *Anopheles quadrimaculatus* Adult Females

Compound	Concentration (ppm)	% Mortality *	Approximate (ppm) LC_{50}
	0.5 1.0 2.0 3.0 5.0 15.0	10 10 5 5 52 95	5
	5.0 10.0 20.0 40.0 80.0	(1) 10 (2) 6 14 26 66 60 62 78 92 90	(1) 21 (2) 18.8

* Data obtained in 2 different trials.

** Disclosed in South African Patent Application 73/4462

(1) = Test one (2) = Test two

Example 27.

Residual insecticidal activity determined for low volume applications of test compounds.

Test compounds were dispersed in 65% acetone—35% water mixtures in sufficient amounts to provide 0.08 kg/ha of compound in 5.1 gallons of water. Cotton plants were then placed in a spray cabinet and sprayed with a stationary overhead sprayer as they passed beneath it.

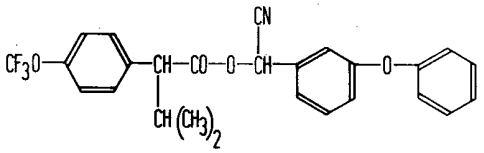
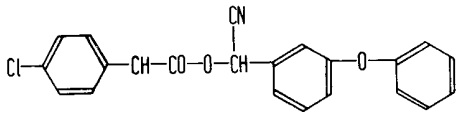
After the leaves had ried, two leaves from each of two plants were excised and placed in petri dishes (90 mm × 10 mm) on moist filter paper. Five third instar tobacco budworm larvae were placed on each leaf and the petri dish capped. The infested dishes were then placed in the holding room with continuous light, ambient temperature of 80°F and 50% r.h. Larval counts were made after 72 hours.

The remaining plants were placed under high intensity lights in the greenhouse. Leaf samples were assayed with third instar tobacco budworm larvae after 3, 7, 10 and 14 days.

Data obtained are reported in Table XI below.

TABLE XI

Residual Insecticidal Activity Against Tobacco Budworms Determined for Low Volume Spray Application on Cotton Plants

Compound	Rate kg/ha	Days Residual Activity									
		0		3		7		10		14	
		1	2	1	2	1	2	1	2	1	2
	0.08	95	.03	100	0	90	.03	90	0	80	.03
	0.08	95	.1	90	3.0	80	2.5	80	0.78	50	1.6
Check	–	0	92.5	0	88.5	0	87.5	30	41.3	0	67.5

1 = Average % Mortality 20 TBW/point (72 Hours Mortality Count)
2 = Average % Feeding Damage/4 Replicates

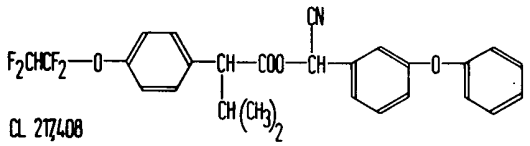
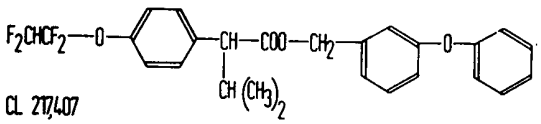
Example 28.

Ixodicidal Activity.

The procedure of Example 22 is employed to demonstrate the ixodicidal activity of compounds of the invention at 12.5, 2.5, 0.5, 0.1, 0.02 or 0.004 ppm concentrations. The results achieved are summarized in Table XII below.

TABLE XII

Percent Larval Tick Mortality of *Boophilus microplus* Larvae

Compound	Days Post-Treatment	Percent Mortality at Conc. (ppm)					
		12.5	2.5	0.5	0.1	0.02	0.004
 CL 217,408	2	100	100	100	100	0	0
	3	100	100	100	100	45	25
 CL 217,407	2	100	100	100	0	0	0
	3	100	100	100	20	15	15

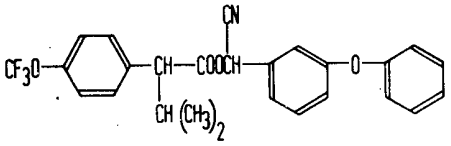
Example 29.

The effectiveness of compounds of the invention for controlling adult multi-host ticks, *Rhipicephalus sanguineus* (R.S.) and *Dermacentor variabilis* (D.V.), of dogs is determined in the following tests, wherein test compound is made up as described in Example 22. Sufficient compound is used to give solutions containing 100, 10 or 1 ppm of test compound.

Adult engorged female ticks are then dipped in the test solutions for 3 seconds and placed in individual containers and held for 48 hours in a room maintained at 80°F. and 50% r.h. At the end of the holding period, the ticks are examined and egg deposits counted. Engorged females that do not deposit eggs are considered dead Data obtained are reported in Table XIII below.

TABLE XIII

Ixodicidal Activity Against Adult
Rhipicephalus sanquineus (R.S.) and *Dermacentor variabilis* (D.V.)

Compound	Concentration in ppm	Percent Adult Tick Mortality	
		R.S.	D.V.
	100	100	100
	10	100	90
	1	100	60

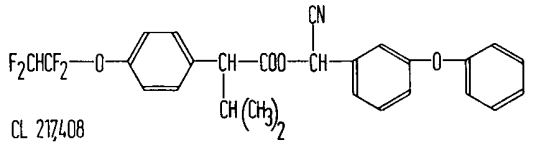
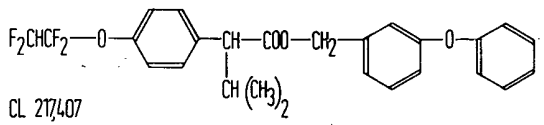
Example 30.

In vitro Adult *Ctenocephalides felis* Test.

In these tests, 10 adult fleas of the species *Ctenocephalides felis* are sprayed for 30 seconds with an acetone/water solution containing 100, 50, 10 or 1 ppm of the test compound. After this treatment, the fleas are maintained for 48 hours at room temperature and 80 + % r.h. at 24 and 48 hours, the fleas are examined and mortality counts made. Data obtained are reported in Table XIV below.

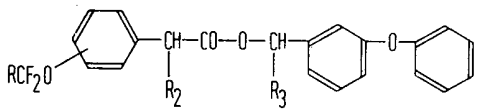
TABLE XIV

Siphonaptericidal Activity of Test Compounds

Compound	Hours Post-Treatment	Percent Mortality at Conc. (ppm)			
		100	50	10	1
 CL 217,408	24 48	100 100	70 90	0 20	0 0
 CL 217,407	24 48	80 90	50 50	0 0	0 0

WHAT WE CLAIM IS:—

1. A compound having the formula:



wherein the substituent RCF_2O— is *m* or *p* to the carbon to which the alkanoic acid ester group is attached and wherein R represents H, F, Cl, CHF_2 or CF_3; R_2

represents ethyl, *n*-propyl, isopropyl, *t*-butyl or isopropenyl; and R_3 represents hydrogen or cyano; or an optical isomer thereof.

2. A compound according to Claim 1, wherein the RCF_2O— group is *p* to the carbon to which the alkanoic acid ester group is attached and R, R_2 and R_3 are as defined in Claim 1.

3. A compound according to Claim 1, wherein the RCF_2O— group is *m*- to the carbon to which the alkanoic acid ester is attached and R, R_2 and R_3 are as defined in Claim 1.

4. A compound according to Claim 2 or Claim 3, wherein R is F; R_3 is CN and R_2 is ethyl, *n*-propyl, isopropyl, *t*-butyl or isopropenyl.

5. The compound, *m*-phenoxybenzyl α - isopropyl - 4 - (1,1,2,2 - tetrafluoroethoxy)phenylacetate.

6. The compound, α - cyano - *m* - phenoxybenzyl α - isopropyl - 4 - (1,1,2,2-tetrafluoroethoxy) - phenylacetate.

7. The compound, α - cyano - *m* - phenoxybenzyl α - isopropyl - 4 - (trifluoromethoxy)phenylacetate.

8. The compound, *m* - phenoxybenzyl α - isopropyl - 4 - (trifluoromethoxy)-phenylacetate.

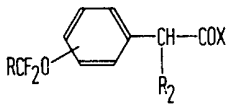
9. A method for controlling insects and acarina, comprising contacting the insects and acarina, their habitat, breeding grounds or feed, with an insecticidally or acaricidally effective amount of a compound according to any preceding claim.

10. A method for the systemic control of insects and acarina that feed on the body fluids of livestock and domestic animals, comprising orally or parenterally administering to the animal host a systemically effective amount of a compound according to any one of Claims 1—8.

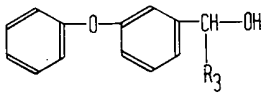
11. A method according to Claim 10, wherein the compound is orally administered to the host animal.

12. A method according to Claim 10, wherein the compound is parenterally administered to the host animal.

13. A method for the preparation of a compound as defined in Claim 1, comprising treating a compound having the structure:



where X is halogen and R and R_2 are as defined in Claim 1; with a *m*-phenoxybenzyl alcohol having the formula:



where R_3 is as defined in Claim 1, in the presence of a tertiary organic amine acid acceptor and an inert organic solvent at a temperature of from 10°C to 30°C.

14. An insecticidal acaricidal composition, comprising a compound according to any one of Claims 1—8 and a solid or liquid carrier therefor.

15. A composition according to Claim 14 for oral or parenteral administration to livestock or domestic animals, wherein the carrier is a pharmaceutically acceptable carrier.

16. A composition according to Claim 14 for use in a method according to Claim 9, wherein the carrier is a liquid and the composition also comprises an emulsifying agent and a surfactant.

17. A compound according to Claim 1 and substantially as described in any one of Examples 7, 8, 15 or 16 herein.

18. A method for controlling insects or acarina, according to Claim 9 and substantially as described in any one of Examples 17—21 or 25—27 herein.

19. An insecticidal or acaricidal composition according to Claim 14 and substantially as described in any one of Examples 17—30 herein.

20. A method for the preparation of a compound as defined in Claim 1, substantially as described in any one of Examples 7, 8, 15 or 16 herein.

21. A compound as defined in Claim 1, whenever prepared by a method according to Claim 13 or Claim 20.

TREGEAR, THIEMANN & BLEACH,
Chartered Patent Agents,
Enterprise House, Isambard Brunel Road, Portsmouth, PO1 2AN,
and
19/51 Bedford Row, London, WC1V 6RL.

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