

Cycloalkyl carboxylic esters, insecticidal compositions containing them, and methods for their preparation

This invention relates to new insecticidal compounds methods of preparing these compounds and to new insecticidal or nematocidal compositions containing the compounds.

Throughout this specification, where the context permits, the word "insect" is used in its broad common usage and includes spiders and mites which are not classed as insects in the strict biological sense. Thus the term implies reference not only to those small invertebrate animals belonging mostly to the class *Insecta*, comprising six-legged, usually winged forms, such as beetles, bugs, flies and the like, but also to other allied classes of arthropods whose members are wingless and usually have more than six legs, such as spiders, wood lice and the like, and especially to the order *Acaridae* which includes the mites and ticks. The words "insecticide" and "insecticidal" are similarly used.

It has long been known that certain naturally occurring compounds that are esters based on chrysanthemic acid are valuable insecticides. Thus for instance the naturally occurring compounds Pyrethrin I and II are known as insecticides and can be extracted from Pyrethrum flowers. Such compounds include a cyclopropyl ring one carbon member of which carries a carboxylic ester substituent. Extensive research has been conducted into the effect of varying the esterifying group to produce a range of commercial or experimental Pyrethroid insecticides.

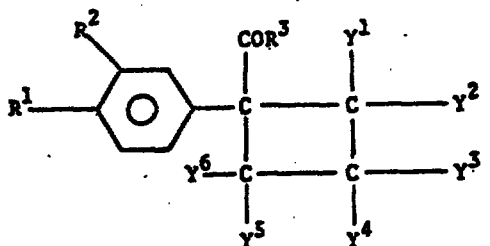
German OS 2653189 describes insecticidal compounds that are esters based on a halogen-substituted cyclopropyl group.

The manufacture of many of the synthetic Pyrethroids is rather difficult to carry out in an economic manner.

It has now been found that compounds based on a cyclobutyl ring, instead of a cyclopropyl ring, can be manufactured more easily than many of the known synthetic Pyrethroids and have very valuable insecticidal activity. These compounds have, on one ring carbon atom, a carboxylic ester group and an aryl group as defined below. Particularly valuable properties, and in particular especially high insecticidal activity, are obtained as a result of one or more of these other ring carbon atoms being substituted by halogen preferably fluorine.

At the time of making the invention it was not publically known that any cyclobutane esters had valuable insecticidal properties. Since making the invention we have become aware of German OS 2733740 which describes compounds related to those of the invention but the specifically described compounds have inferior properties to the preferred compounds of the invention.

The compounds provided by this invention have the general formula I

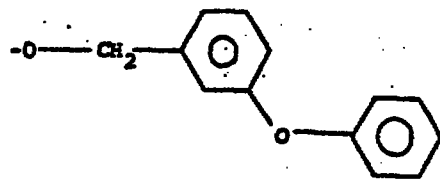


wherein R¹ is hydrogen or a methoxy, ethoxy, propoxy, butoxy, tetrafluoroethoxy, methylthio, ethylthio, propylthio, fluoro, chloro, bromo, methyl, ethyl, or nitro group, and R² is hydrogen or a methyl group, or R¹ and R² together form a methylenedioxy group, and R³ is hydroxy, chloro or an esterifying group, and Y¹, Y², Y³, Y⁴, Y⁵ and Y⁶ are the same or different groups and each is hydrogen or a fluoro, bromo or chloro group, at least one being fluoro bromo or chloro. The invention includes of course not only the free acid (R³ is hydroxy) but also equivalent derivatives, such as salts with organic or inorganic bases, e.g. salts with sodium or other alkali metals.

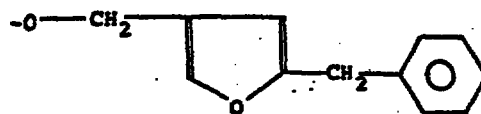
The esterifying group may be a lower alkoxy group. Throughout this specification, any lower alkoxy or lower alkyl group contains 8 or less, and preferably 4 or less, carbon atoms. However other esters that are equivalent from the point of view of the utility of the esters as intermediates in the synthesis of insecticidally active compounds, e.g. cycloalkyl are included.

Compounds in which R³ is hydroxy, chlorine or a simple esterifying group are of primary value as intermediates in the synthesis of insecticidal compounds in which the esterifying group is one that contributes to the insecticidal activity of the products. Preferred insecticidal esterifying groups are selected from the following groups (a) to (f):—

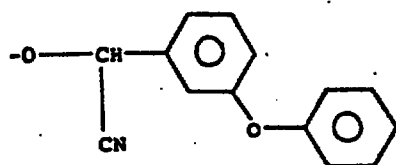
(a)



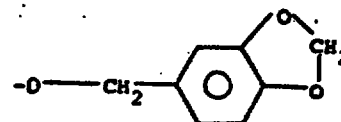
(b)



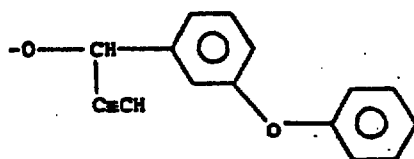
(c)



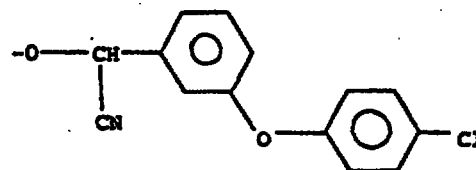
(d)



(e)



(f)



The acids of the present invention (formula I $R^3 = OH$) and their esters are novel. Preferably R^1 is methoxy, ethoxy or propoxy group and R^2 is hydrogen. Compounds in which R^1 and R^2 form the methylenedioxy group are also preferred.

Preferably also, R^3 is one of groups (a), (c) and (e) as defined above.

It is also preferred that from one to all six of the groups Y^1 to Y^6 is a fluoro group, the remainder (if any) being hydrogen. Tetrafluoro-substitution ($Y^1, Y^2, Y^3, Y^4 = F; Y^5, Y^6 = H$) is especially preferred.

Specifically preferred compounds in accordance with the invention are as follows:—

3' - phenoxybenzyl 1 - (3,4 - methylenedioxyphenyl) - 2,2,3,3 - tetrafluorocyclobutanecarboxylate, and its α -cyano and α -ethynyl derivatives;

3' - phenoxybenzyl 1 - (4 - ethoxyphenyl) - 2,2,3,3 - tetrafluorocyclobutane carboxylate, and its α -cyano and α -ethynyl derivatives.

The compounds of formula I in which R^3 is one of groups (a) to (f) are extremely active as insecticides, having an insecticidal activity an order of magnitude greater than most known insecticides. These compounds also possess the property of contact repellency to insects. The compounds are generally more active against flies than the compounds of German OS 2653189.

The compounds of formula I in which $R^3 = OH$ or lower alkoxy are useful as intermediates in the preparation of the other esters with $R^3 = (a)$ to (f) as shown below.

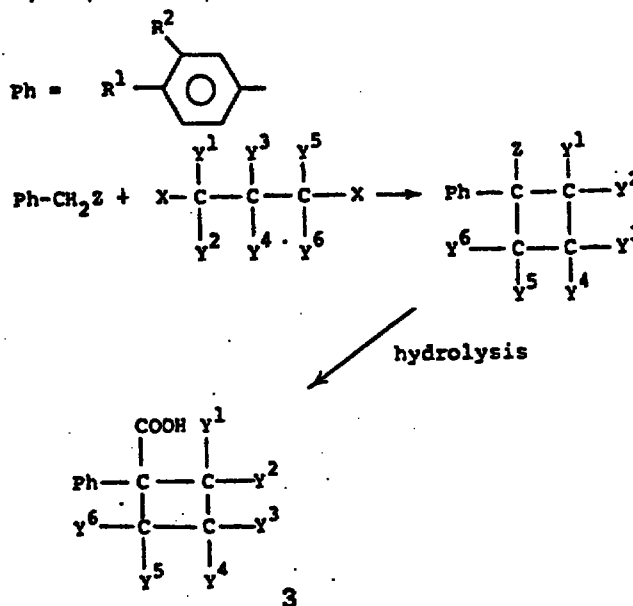
The compounds of formula I are optically active and can be resolved into their optical isomers by conventional methods. The invention thus includes the individual (+) and (−) optical isomers of the compounds as well as the racemic ($\pm$) forms.

It should also be noted that the insecticidal activities of the optical isomers of the compounds I with $R^3 = (a)$ to (f) may differ by an order of magnitude or more.

The invention also includes methods for the synthesis of the compounds I.

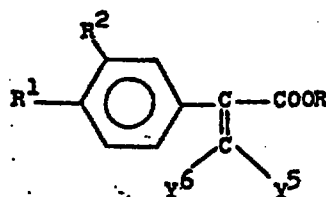
The compounds I in which R^3 is one of the groups (a) to (f) may be prepared by esterification of the free acid (formula I, $R^3 = OH$) with the appropriate alcohol R^3H , wherein R^3 is one of the groups (a) to (f). Such esterification may be carried out by any suitable known method, e.g., by direct reaction or by prior conversion of the acid and/or the alcohol to a suitable reactive derivative, or by an ester interchange reaction between the alcohol R^3H ($R^3 = (a)$ to (f)) and a lower alkyl ester of the acid.

The acid (formula I, $R^3 = OH$) is prepared by the reaction of an appropriately substituted benzyl compound with an appropriately substituted 1,3-dihalopropane to form a 1-phenylcyclobutane compound which can be hydrolysed to the acid. This reaction scheme is as follows:



where Z represents a group which activates the benzylic methylene and is itself later hydrolysable to a carboxyl group, e.g., $-\text{C}\equiv\text{N}$ or $-\text{COOEt}$; X represents a chloro, bromo or iodo group; R^1 , R^2 , Y^1 , Y^2 , Y^3 , Y^4 , Y^5 , and Y^6 are as defined above.

An alternative method of preparation of the acid (formula I, $\text{R}^3 = \text{OH}$) as its lower alkyl ester is by addition of the olefin $\text{Y}^1\text{Y}^2\text{C} = \text{CY}^3\text{Y}^4$ to the substituted phenylacrylic ester of formula II



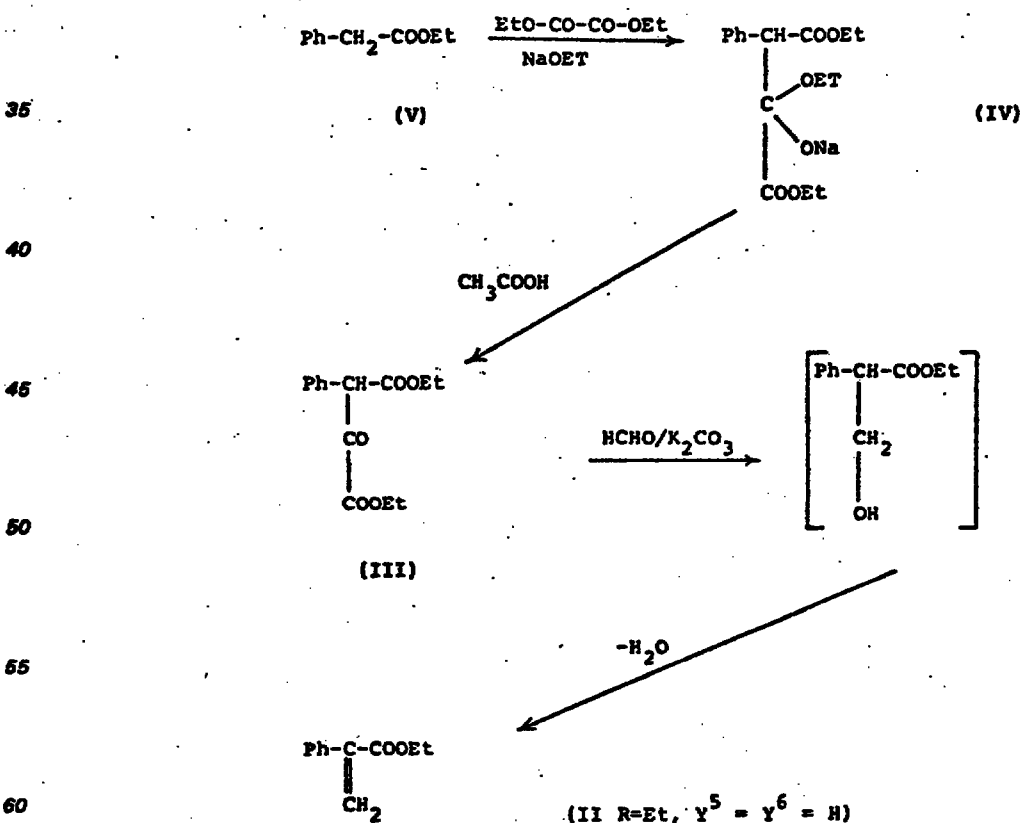
where R is an alkyl group containing up to 8 carbon atoms and R^1 , R^2 , Y^1 , Y^2 , Y^3 , Y^4 , Y^5 and Y^6 are as defined above.

Esters of formula I ($\text{R}^3 = \text{lower alkoxy}$) wherein $\text{Y}^3 = \text{Y}^4 = \text{F}$ and $\text{Y}^1 = \text{Y}^2 = \text{Y}^5 = \text{Y}^6 = \text{H}$ can be made by first preparing the compounds wherein $\text{Y}^3 = \text{Y}^4 = \text{F}$, $\text{Y}^1 = \text{Y}^2 = \text{Cl}$ according to the preceding method (using dichlorodifluoroethylene) and then hydrogenating the product to replace the chlorine groups by hydrogen.

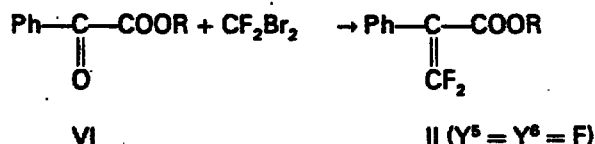
The esters II wherein $\text{Y}^5 = \text{Y}^6 = \text{H}$ may be obtained according to the following general procedure:

- (1) A lower alkyl ester of the appropriately substituted phenylacetic acid (V) is condensed with a di(lower alkyl) oxalate in the presence of a solvent and a basic catalyst, to produce a solution of an enolate salt (IV).
- (2) The solution of the enolate salt is acidified to give the corresponding phenyloxaloacetate (III).
- (3) The compound III is reacted with formaldehyde under alkaline conditions to give the phenyl hydroxymethyl acetate which on dehydration (sometimes spontaneously) yields the phenylacrylic ester (II).

This reaction sequence is illustrated in the following overall reaction scheme. It will be appreciated that the specific acids and bases indicated may be replaced by other suitable compounds. Also lower alkyl esters, other than the ethyl esters shown may be employed.

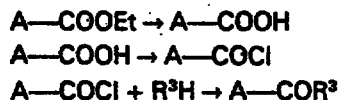


When $Y^5 = Y^6 = F$, the esters II can be made according to the method described by D.G. Nae and D.J. Burton, *Synthetic Communications*, 3, 197—200 (1973). In this method the appropriate phenyl keto ester of formula VI is reacted with dibromodifluoromethane (CF_2Br_2) in the presence of 2 moles of tris(dimethylamino)phosphine and a suitable solvent such as diglyme or triglyme

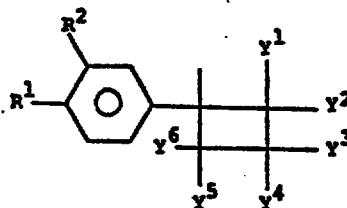


where Ph is as defined above and R is a lower alkyl group.

The general approach to formation of the active esters of the invention is as follows:—

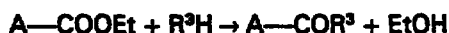


where A is



R^1 , R^2 , Y^1 , Y^2 , Y^3 , Y^4 , Y^5 and Y^6 are as defined above and R^3 is one of the groups (a) to (f) defined above.

Alternatively the ethyl ester can be directly converted as follows:—



The active compounds described herein may be dissolved in a suitable organic solvent, or mixture of solvents, to form solutions or brought into aqueous suspension by dispersing organic solvent solutions of the compounds in water, to provide useful liquid compositions, which may be incorporated, for example, into aerosol-type dispersions with the usual propellants. The active compounds may also be incorporated in solid compositions which may include inert solid diluents or carriers, to form useful solid compositions. Such compositions may also include other substances such as wetting, dispersing or sticking agents, and may be prepared in granular or other forms to provide slow release of the compounds over an extended period of time. The compounds may be employed in such compositions either as the sole toxic agent or in combination with other insecticides such as pyrethrum, rotenone, or with fungicidal or bactericidal agents, to provide compositions useful for household and agricultural dusts and sprays, textile coating and impregnation, and the like.

In particular, the active compounds of the invention may be advantageously combined with other substances which have a synergistic or potentiating action. Generally such substances are of the class of microsomal oxidase inhibitors i.e., they inhibit the detoxification of insecticides in insects produced by the action of oxidative enzymes. Typical substances of this type are the pyrethrin synergists of which the following are examples:—

	Common Name	Chemical Name
5	Piperonyl butoxide	α -[2-(2-butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-propyl-toluene
	Piperonyl cyclonene	3-hexyl-5(3,4-methylenedioxy-phenyl)-2-cyclohexanone
10	"Sesoxane" (Sesamex)	2-(3,4-methylenedioxy-phenoxy)-3,6,9-trioxaundecane
15	"Sulfoxide"	1,2-(methylenedioxy)-4-[2-(octylsulfinyl)propyl]-benzene
20	n-Propyl isome	dipropyl 5,6,7,8-tetrahydro-7-methylnaphtho-[2,3-d]-1,3-dioxole-5,6-dicarboxylate

("Sesoxane," "Sesamex" and "Sulphoxide" are Registered Trade Marks).

We have found that "Sesoxane" (made by Shulton Inc., Clifton, N.J., U.S.A.) is particularly useful as a potentiator. The amount of "Sesoxane" used may vary from 1/1000th to five times the weight of the compound the preferred range being from about 1/100th to an equal part by weight. Piperonyl butoxide also is a useful potentiator in similar amounts.

The preparation and properties of the compounds of the invention are illustrated by the following specific examples. It should be noted, of course, that these examples are intended to be illustrative of the methods and procedures utilized in preparing the compounds and that they are not intended to be restrictive or to be regarded as embodying the only way in which the compounds can be formed and recovered.

Example 1 (Prior Art Compound)

(a) 1-(4-chlorophenyl)cyclobutane nitrile

4-Chlorobenzyl cyanide (10 g) in dry DMSO (20 ml) was added over 5 min to a stirred suspension of sodium hydride (4.4 g) in DMSO at 25°C under argon. The mixture was stirred for 30 minutes then a solution of 1,3-dibromopropane (27 g) in dry DMSO (50 ml) was added over 30 minutes while maintaining the temperature of the reaction mixture at 25—30°C. After stirring an additional 40 minutes at this temperature the reaction mixture was added to ice water (500 ml) and extracted with dichloromethane (3 x 75 ml). The extracts were evaporated and the residue extracted with diethyl ether (4 x 50 ml). The ether extracts were washed with water, dried over anhydrous sodium sulphate and evaporated to yield an oil (10.8 g) which on distillation gave the nitrile [bp 90°C/10⁻⁶ Torr.] yield 5.4 g (43%). Analysis: C 68.48% H 5.49% Cl 18.3%. C₁₁H₁₀Cl N requires: C 68.93% H 5.26% Cl 18.5%.

(b) 1-(4-chlorophenyl)cyclobutane carboxylic acid

1-(4-chlorophenyl)cyclobutane nitrile (5 g) was mixed with ethylene glycol (60 ml) and 40% w/w aqueous potassium hydroxide solution (80 ml) and refluxed under argon for 18 hours. The mixture was cooled, added to ice water and extracted with diethyl ether. The aqueous layer was acidified and the precipitate was filtered off, washed with water, dried and recrystallised from petroleum ether (b.p. 40—60°C) to give the acid as white needles mp 88—9°C, yield 4.5 g (82%). Analysis: C 62.70% H 5.14% Cl 16.5% O 15.2%. C₁₁H₁₁ClO₂ requires: C 62.72% H 5.26% Cl 16.83% O 15.2%.

(c) 3'-phenoxybenzyl 1-(4-chlorophenyl)cyclobutanecarboxylate

1-(4-Chlorophenyl)cyclobutane carboxylic acid (1 g) was dissolved in thionyl chloride (1 ml) and heated at reflux for 40 minutes. Excess thionyl chloride was removed in vacuo and the residue was taken up in petroleum ether 40—60°C (40 ml) and added over 15 minutes to a stirred mixture of 3-phenoxybenzyl alcohol (1.1 g), pyridine (1 ml), benzene (50 ml) and petroleum ether 40—60°C (50 ml) maintained at 10°C. The mixture was stirred at 20—25°C for 3 hours then added to ice water, washed with 0.5M hydrochloric acid, water, dilute sodium bicarbonate solution and dried over anhydrous sodium sulphate. The solvent was evaporated to give an oil (2.3 g) which after chromatography on silica gel, eluting with benzene/petroleum ether, gave the ester 1.52 g (82%) Analysis: C 72.87% H 5.30% Cl 9.2% O 12.1% C₂₄H₂₁ClO₃ requires C 73.37% H 5.39% Cl 9.0% O 12.2%.

Example 2 (comparative)

(a) 1-(4-ethoxyphenyl)cyclobutane carboxylic acid

Ethyl 4-ethoxyphenylacetate (14 g) in anhydrous diethyl ether (20 ml) was added to a stirred suspension of sodamide (5.3 g) in liquid ammonia (400 ml) over 3 minutes and the mixture stirred for an additional 20 minutes. 1,3-dibromopropane (14 g) in diethyl ether (10 ml) was added over 20 minutes and the mixture stirred for 17 hours. 50 ml of saturated ammonium chloride solution was added and the reaction mixture extracted with diethyl ether. Evaporation of the solvent gave a residue (17.4 g) which after chromatography on silica gel by eluting with benzene/chloroform gave an oil (7.2 g). The oil was dissolved in ethanol (50 ml) and 10% sodium hydroxide solution (50 ml) was added. The mixture was refluxed for 3 hours, cooled, added to ice water and extracted with diethyl ether. The aqueous layer was acidified and the precipitate was filtered off, washed with water, dried and recrystallised from petroleum ether 40—60°C to give the acid 5.2 g (35%) mp 90—1°C. Analysis: C 71.04%, H 7.23% O 22.0% $C_{13}H_{16}O_3$ requires C 70.89% H 7.32% O 21.8%.

15 (b) 3'-phenoxybenzyl 1-(4-ethoxyphenyl)cyclobutane carboxylate

1-(4-ethoxyphenyl)cyclobutane carboxylic acid (1 g) was refluxed in thionyl chloride (1 ml) for 30 minutes and the excess thionyl chloride removed in vacuo. The residue was taken up in petroleum ether 40—60°C (25 ml) and added over 5 minutes to a stirred mixture of 3-phenoxybenzyl alcohol (1.1 g), pyridine (1 ml), benzene (25 ml) and petroleum ether 40—60°C (25 ml) at 15°C. The mixture was stirred at 15°C for 3 hours, then added to ice water and extracted with diethyl ether. The extract was washed with water, 0.5M hydrochloric acid, and sodium bicarbonate solution then dried over anhydrous sodium sulphate and the solvent removed to give an oil (2.1 g). Chromatography on silica gel, eluting with benzene, gave the ester 1.5 g (82%). Analysis: C 77.55% H 6.65% O 16.0% $C_{26}H_{26}O_4$ requires C 77.59% H 6.51% O 15.9%.

Example 3

(a) 2-(4-ethoxyphenyl)propenoic acid ethyl ester

This part of the example shows the general method of forming the 2-aryl-acrylic acid esters. (Formula II)

Alcohol-free sodium ethoxide freshly prepared from sodium (13.9 g) and excess ethanol was slurried in dry benzene (200 ml). To this suspension diethyl oxalate (88.5 g) was added over 15 minutes. Ethyl-p-ethoxyphenylacetate (V) (114.2 g) was added to the resulting clear yellow solution over 30 minutes at room temperature. After a further 1 hour period the reaction mixture solidified. The solid, sodium diethyl - 2 - p - ethoxyphenyl - 3 - ethoxy - 3 - oxido - oxaloacetate (IV) was triturated and washed well with ether. The combined ether washings were evaporated to a small volume to obtain a second crop of the salt.

The combined yield was 227.4 g.

The sodium salt was acidified by adding it in portions to a well stirred emulsion of equal parts of diethyl ether and dilute acetic acid (approximately 10%). After separation the ether layer was washed with water and dilute sodium bicarbonate solution, and dried with anhydrous sodium sulphate. After evaporation of the ether, the resulting oil was crystallized from petroleum ether (b.p. 60°—80°C), to yield diethyl - 2 - p - ethoxyphenyloxaloacetate (III) 143.8 g (85%), m.p. 59—60°C.

The keto-ester III (143.8g) was stirred in dilute formaldehyde solution (62 ml 37% formaldehyde + water 220 ml) and to the suspension potassium carbonate solution (54.5 g, in water 280 ml) was added dropwise. At the end of the addition, ether was added to the stirred suspension to dissolve the gummy precipitate which formed and after an additional 15 minutes, gas evolution commenced. When this gas evolution ceased (after about 2 hours) the reaction mixture was extracted with additional ether and the combined ether extracts were washed with water and evaporated after drying with Na_2SO_4 . The yield of the ethyl 2-(4-ethoxyphenyl) propenoate (II) (isolated as a yellow oil) was 97.8 g (79.8%).

(b) Ethyl 1-(4-ethoxyphenyl)-2,2,3,3-tetrafluorocyclobutane carboxylate

2-(4-ethoxyphenyl)propenoic acid ethyl ester (13.2 g) was mixed with benzene (7.5 ml), α -pinene (2 drops) N-ethyl-diisopropyl amine (2 drops) and tetrafluoroethylene (15.5 ml) and heated to 150—155°C for 24 hours then 155—60°C for 17 hours. After evaporation of volatile materials the residue (16.6 g) was dissolved in dichloromethane and chromatographed on a column of silica gel to give the ester as a colourless oil 14.5 g (75%). Analysis: C 56.47%, H 5.24%, F 23.4%. $C_{15}H_{16}F_4O_3$ requires C 56.25%, H 5.04%, F 23.7%.

60 (c) 1-(4-ethoxyphenyl)-2,2,3,3-tetrafluorocyclobutane carboxylic acid

Ethyl 1-(4-ethoxyphenyl)-2,2,3,3-tetrafluorocyclobutane carboxylate (14.5 g) was dissolved in ethanol (100 ml) and a 10% w/w solution of sodium hydroxide in water (100 ml) was added and the mixture refluxed for 2.5 hours. The mixture was cooled, added to ice water and extracted with diethyl ether. The aqueous layer was acidified and the precipitate was filtered off, washed with water, dried

and crystallised from 60—80°C petroleum ether to give the acid mp 112—3°C. Yield 11.2 g (85%). Analysis: C 53.20% H 4.22% F 25.9% $C_{13}H_{12}F_4O_3$ requires C 53.43% H 4.14% F 26.0%.

(d) *3'-phenoxybenzyl 1-(4-ethoxyphenyl)-2,2,3,3-tetrafluorocyclobutane-carboxylate*

1-(4-ethoxyphenyl)-2,2,3,3-tetrafluorocyclobutane carboxylic acid (0.9 g) was refluxed with thionyl chloride (1 ml) for 45 minutes and the excess thionyl chloride was removed in vacuo. The residue was dissolved in petroleum ether 40—60°C (40 ml) and added over 5 minutes to a mixture of 3-phenoxybenzyl alcohol (1 g), pyridine (1 ml), benzene (25 ml), and petroleum ether 40—60°C (25 ml) maintained at 20°C. The mixture was stirred for 3 hours then added to ice water and extracted with diethyl ether. The extract was washed with water, 0.5M hydrochloric acid, and sodium bicarbonate solution, dried over anhydrous sodium sulphate and the solvent evaporated to give an oil (2 g). Chromatography on silica gel by eluting with benzene gave the ester 1.2 g (82%). Analysis: C 65.45%, H 4.84% F 16.0%. $C_{26}H_{22}F_4O_4$ requires C 65.82%, H 4.67%, F 16.0%.

Example 4

(a)(-)*Enantiomer of 1-(4-ethoxyphenyl)-2,2,3,3-tetrafluorocyclobutane carboxylic acid*

$\alpha(+)$ -(1-naphthyl)ethylamine was added to a solution of the racemic acid (2 g) (prepared as in Example 3(c)) in ethyl acetate (75 ml) and n-hexane. The salt which formed was crystallized four times from ethyl acetate at room temperature. The (+)(-) salt was decomposed with hydrochloric acid (1M) and the residue recrystallized twice from ethanol. The (-) acid which had $\alpha_{20}^D = -118.2^\circ$ and m.p. 194°C was obtained in 15% yield.

(b) (-)*3'-Phenoxybenzyl 1-(4-ethoxyphenyl)-2,2,3,3-tetrafluorocyclobutane carboxylate*

The resolved (-) acid, 0.2 g., was refluxed in thionylchloride (1 ml) for one hour. After evaporation of excess thionyl chloride, the residue was dissolved in petroleum ether (b.p. 60—80°C) and added to 3-phenoxybenzyl alcohol (0.139 g) and pyridine (0.238 g) in benzene (3 ml) and petroleum ether (3 ml). The reaction mixture was stirred overnight, quenched with ice-water, washed with water and the solvent layer separated and dried over molecular sieve. After evaporation of the solvent the pure ester was obtained as a viscous liquid by chromatography in silica gel using methylene chloride as the eluent. Yield 99.1%, $\alpha_{20}^D = -58.2^\circ$.

Example 5

(a) *1-(3,4-methylenedioxyphenyl)-2,2,3,3-tetrafluorocyclobutane carboxylic acid*

A mixture of ethyl 2-(3,4-methylene dioxyphenyl) propenoate (2.2 g), tetrafluoroethylene (5 ml.), α -pinene (1 drop), N-ethyl-diisopropylamine (1 drop) and benzene (10 ml), was heated at 150—155°C for 24 hours then at 160—165°C for 16 hours, then cooled. The solvent was evaporated to leave an oil (3.0 g). This oil was purified by chromatography on silica gel using benzene as eluent to give 1.4 g (44%) of ethyl 1 - (3,4 - methylene dioxyphenyl) - 2,2,3,3 - tetrafluorocyclobutane carboxylate.

The ethyl ester was hydrolysed by refluxing for 2 hours with a mixture of potassium hydroxide (5 g), water (50 ml) and ethanol (50 ml). The ethanol was removed by evaporation and the aqueous residue extracted with diethyl ether. The aqueous layer was acidified and the precipitate filtered off, dried and recrystallized from petroleum spirit (b.p. 60—80°C)/diethyl ether to yield 0.9 g of the acid as white crystals m.p. 168—9°C. Analysis: C 49.62%, H 2.72%, F 25.8%. $C_{12}H_8F_4O_4$ requires 49.33%, H 2.76%, F 26.0%.

(b) *3'-phenoxybenzyl 1-(3,4-methylenedioxyphenyl)-2,2,3,3-tetrafluorocyclobutane carboxylate.*

The acid prepared in Example 5(a) (0.5 g) was mixed with thionyl chloride (1 ml) and refluxed for 45 minutes. Excess thionylchloride was removed under vacuum. The residue was dissolved in petroleum spirit (b.p. 40—60°C) (5 ml), and added over 5 minutes to a stirred mixture of 3-phenoxybenzylalcohol (0.4 g), pyridine (0.5 ml), benzene (15 ml) and petroleum spirit (b.p. 40—60°C) (15 ml). After overnight stirring at room temperature the mixture was added to ice water and extracted with diethyl ether. The ether extract was washed with dilute hydrochloric acid, water, sodium bicarbonate solution and dried over anhydrous sodium sulphate. Evaporation of the ether left an oily residue (0.78 g) which was purified by chromatography on silica gel with benzene as eluent to yield 0.7 g of the 3-phenoxy benzyl ester as a clear yellow oil. Analysis: C 63.54%, H 4.01%, F 15.9%. $C_{25}H_{18}F_4O_5$ requires C 63.30%, H 3.82%, F 16.0%.

Examples 6 to 22

Using the general method set out in Example 3, the compounds listed in Table 1 were obtained from the appropriate starting materials.

Analysis, spectra and other characterising data were consistent with the stated structures. Table 1 includes the compounds of Examples 1, 2, 3, 4 and 5 for ease of reference.

TABLE 1

Example No.	R ¹	R ²	Y ¹	Y ²	Y ³	Y ⁴	Y ⁵	Y ⁶	R ³
5	1	Cl	H	H	H	H	H	H	(a)
	2	C ₂ H ₅ O	H	H	H	H	H	H	(a)
10	3	C ₂ H ₅ O	H	F	F	F	F	H	(a)
	4*	C ₂ H ₅ O	H	F	F	F	F	H	(a)
	5	—O—CH ₂ —O—	F	F	F	F	H	H	(a)
15	6	CHF ₂ CF ₂ O	H	F	F	F	F	H	(a)
	7	C ₂ H ₅ O	H	F	F	F	F	H	(c)
20	8	Cl	H	F	F	F	F	H	(b)
	9	C ₂ H ₅ O	H	F	F	F	F	H	(d)
	10	C ₂ H ₅ O	H	F	F	F	F	H	(b)
25	11	Cl	H	F	F	F	F	H	(a)
	12	CH ₃ O	H	F	F	F	F	H	(a)
30	13	—O—CH ₂ —O—	F	F	F	F	H	H	(c)
	14	C ₂ H ₅ O	H	F	F	F	F	H	(f)
	15	Cl	H	F	F	F	F	H	(c)
35	16	C ₂ H ₅ O	H	H	H	F	F	H	(c)
	17	C ₂ H ₅ O	H	H	F	F	F	H	(c)
40	18	Cl	H	F	Cl	F	F	H	(c)
	19	Cl	H	F	F	F	F	H	(e)
	20	C ₂ H ₅ O	H	Cl	Cl	F	F	H	(c)
45	21	F	H	F	F	F	F	H	(e)
	22	C ₂ H ₅ O	H	F	F	F	F	F	(e)

50 Note* The compound of Example 4 is the R(—) optical isomer of the compound of Example 3.

Example 23

The biological activity of the new cyclobutane esters was examined in a series of tests, the results of which are collected in Table 2.

55 Insecticidal activity was investigated against the common housefly, *Musca domestica*, and the sheep blowfly, *Lucilia cuprina*. The methods used were as follows:—

(i) Housefly

(a) Compound alone

60 Tests were carried out using a standard DDT-susceptible strain (WHO/IN/1) of *M. domestica*. The compound was applied in an acetone solution by microsyringe to the dorsum of the thorax of two-day old female flies reared from the pupae of average weight 2.2—2.5 gm/100 pupae. The adult flies were fed on water and sugar-only diet and maintained at 26°C and 70% RH. The mortalities were counted at 48 hours after treatment and compared with acetone-treated controls. Flies unable to move or stand 65 normally were considered dead. The LD₅₀ value was obtained from a logit computer programme based

on three replicates of 10 flies at each dose level. The LD₅₀ value for DDT determined under the same conditions was 0.26 µg/fly.

(b) *Potentiation*

5. The compound was also tested on the insects described above in conjunction with the potentiator "Sesoxane" by pretreating the insect with 1 µg of the potentiator in acetone.

The mortalities were counted at 48 hours after treatment and compared with acetone and acetone/potentiator controls.

- 10 The LD₅₀ value was determined as described above. For DDT, with the same potentiator the LD₅₀ value as 0.24 µg/fly.

About the same levels of potentiation were obtained when "Sesoxane" were replaced by an equal amount of piperonyl butoxide.

(c) *Insect Repellency*

- 15 Repellency tests were carried out on the same strain of housefly as in the mortality tests. Female flies at least two days old, not previously fed protein, were taken the day before the test, anaesthetized with CO₂ and counted into holding containers of twenty flies each. These were supplied with water and solid sucrose. On the day of the tests the food and water were removed in the morning (0900 hr). As the tests were performed only between 1200 hr and 1730 hr, the flies were therefore starved for a

- 20 minimum of three hours before testing. The test involved the use of attractant baits to which the candidate compound was applied. These were exposed to the flies and the number of flies landing on each bait counted. The baits consisted of aluminium caps of area 5.94 cm² filled with baker's yeast mixed with water and slightly heated to form a solid surface film.

- 25 Eight lots of 20 flies were used in a run in which seven discs were treated with a graded dilution series of the test chemical using acetone as solvent, together with one disc treated with acetone as a control. The concentrations of the compounds ranged from 0.031 µg/µl doubling at each level up to 2.0 µg/µl. One hundred microlitres of each solution was pipetted evenly over the surface of each disc and left until the acetone had evaporated.

- 30 The flies to be used were released into standard 205 mm x 205 mm x 255 mm mesh cages and left to acclimatize in the test room maintained at a temperature of 26°C + 1°C and humidity approximately 60%, for ten minutes before introducing the treated discs into each cage. Before use the discs were marked on the reverse sides and then randomly mixed to avoid bias in counting. In the thirty minute period of the test the number of flies on the surface of each disc was counted in the first and

- 35 second minute after introducing the baits and thereafter every two minutes. In this way sixteen counts were obtained for each concentration, the totals of which were then used for a regression analysis of the concentration effect. Also a total number of landings for each concentration was obtained and used for calculation of the Index of Repellency (IR). All replicate tests were carried out with fresh flies and baits, and the compounds were tested in three replicate runs.

- 40 The total number of flies counted on each disc for the seven concentration levels was summed and averaged. In the following formula this figure is designated (N), where (C) equals the number of flies counted on the control:—

$$45 \quad \frac{C - N}{C + N} \times 100 = \text{Index of Repellency (IR)}$$

(ii) *Sheep Blowfly*

(a) *Insecticidal Activity*

- 50 The compounds were tested for activity against a dieldrin susceptible strain (LBB) which had been collected before dieldrin usage in the field.

- The test compound was applied in acetone solution, 0.5 µl dispensed with a Drummond micropipette to the dorsum of the thorax of 2—3-day old females. Adult flies were fed on water and sugar only and maintained at 25°C and 60—70% RH. The mortalities were determined after 24 hours.

- 55 Moribund flies were regarded as dead. The LD₅₀ values, in terms of concentration, were interpolated from a probit/log dose graph using a computer program.

Comparative LD₅₀ figures for DDT and dieldrin are 0.17 and 0.25 µg/insect.

(b) *Potentiation*

- 60 Potentiation with "Sesoxane" was investigated as described above in the housefly tests.

(c) *Repellency*

Repellency was determined as described above in the housefly tests, except that the baits consisted of an agar gel containing fresh beef blood.

65

TABLE 2
INSECTICIDAL ACTIVITY

Compound of Example No.	Sheep Blowfly (<i>Lucilia cuprina</i>)		
	LD ₅₀ μg/♀ insect	LD ₅₀ with synergist μg/♀ insect	Repellency Index
1	1.78	0.04	36
2	0.77	0.06	61
3	0.05	0.001	79
4	0.024	0.00026	73
5	0.04	0.003	66
6	0.40	0.04	
7	0.02	0.0004	62
8	0.023	0.0023	77
9	0.11	0.03	88
10	0.03	0.003	78
11	0.05	0.007	
12			17
13	0.03	0.001	68
14	0.14	0.009	42
15	0.18	0.006	
16	0.10	0.001	
17	0.14	0.002	
18	0.14	0.001	
19	0.028	0.002	
20	0.22	0.002	

TABLE 2
INSECTICIDAL ACTIVITY (Continued)

Compound of Example No.	Housefly (Musca domestica)		
	LD ₅₀ μg/♀ insect	LD ₅₀ with synergist μg/♀ insect	Repellency Index
1	1.8	0.2	49
2	1.32	0.22	81
3	0.13	0.003	81
4	0.10	0.005	86
5	0.26	0.017	
6	0.6	0.036	12
7	0.18	0.065	89
8	0.55	0.01	
9	0.58	0.05	
10	0.13	0.005	84
11	0.34	0.018	
12	>32	0.24	18
13	0.12	0.018	78
14	0.07	0.005	65
15	0.26	0.6	

Example 24

The following are examples of insecticidal compositions in accordance with the invention. All parts are by weight.

(a) *Spray formulation*

The following composition is adapted for spray application.

Compound of formula I	4.0
"Sesoxane or Piperonyl butoxide	1.0
Deoderized kerosene	79.4
Alkylated naphthalene	16.0

(b) *Aerosol*

The following materials are metered into a suitable 'bomb' container sealed and equipped with a valve in the usual way.

5	Compound of formula I	3.0
	Potentiator	1.0
	Methylene chloride	10.0
10	'Freon 12'	43.0
	'Freon 11'	43.0

Freon is a Trade Mark

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(c) *Water dispersible powder*

The following powdered composition is intended for dispersing in water for application as a spray.

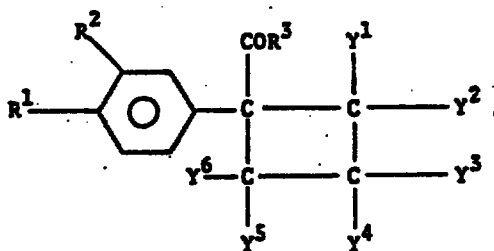
20	Compound of formula I	50.0
	Synthetic fine silica	30.0
	Alkyl aryl sodium sulphonate	1.5
25	Methyl cellulose (15 cp.)	.25
	Attapulgate	8.25

30 **Claims**

1. A compound of the general formula I:—

35

40



wherein R¹ is hydrogen or methoxy, ethoxy, propoxy, butoxy, tetrafluoroethoxy, methylthio, ethylthio, propylthio, fluoro, chloro, bromo, methyl, ethyl, or nitro and R² is hydrogen or methyl, or R¹ and R² together form a methylenedioxy group; R³ is hydroxy, chloro or an esterifying group and Y¹, Y², Y³, Y⁴, Y⁵ and Y⁶ are the same or different groups and each is hydrogen or a fluoro, bromo or chloro, at least one of Y¹, Y², Y³, Y⁴, Y⁵ and Y⁶ being fluoro, bromo or chloro; or a salt of a compound where R³ is hydroxy with an organic or inorganic base.

2. A compound as claimed in claim 1 characterised in that R¹ is a methoxy, ethoxy or propoxy group and R² is hydrogen, or R¹ and R² together form a methylenedioxy group.

3. A compound as claimed in claim 1 or claim 2, characterised in that from one to all six of the groups Y¹ to Y⁶ is a fluoro group, the remainder (if any) being hydrogen.

4. A compound as claimed in claim 3, characterised in that Y¹, Y², Y³ and Y⁴ are all fluoro and Y⁵ and Y⁶ are hydrogen.

5. A compound according to any preceding claim characterised in that R¹ is chloro, fluoro, ethoxy or tetrafluoroethoxy and R² is hydrogen or R¹ and R² together form a methylenedioxy group.

6. A compound according to any of claims 1 to 5 characterised in that it is in the (—) form.

7. A compound according to any of claims 1 to 6 characterised in that R³ is alkoxy containing up to 8 carbon atoms.

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(b) *Aerosol*

The following materials are metered into a suitable 'bomb' container sealed and equipped with a valve in the usual way.

5	Compound of formula I	3.0
	Potentiator	1.0
	Methylene chloride	10.0
10	'Freon 12'	43.0
	'Freon 11'	43.0

Freon is a Trade Mark

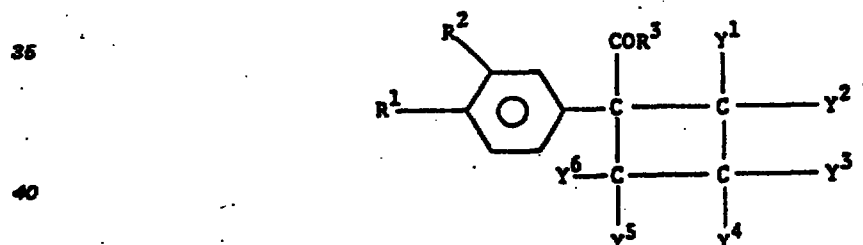
15 (c) *Water dispersible powder*

The following powdered composition is intended for dispersing in water for application as a spray.

20	Compound of formula I	50.0
	Synthetic fine silica	30.0
	Alkyl aryl sodium sulphonate	1.5
25	Methyl cellulose (15 cp.)	.25
	Attapulgate	8.25

30 Claims

1. A compound of the general formula I:—



wherein R¹ is hydrogen or methoxy, ethoxy, propoxy, butoxy, tetrafluoroethoxy, methylthio, ethylthio, propylthio, fluoro, chloro, bromo, methyl, ethyl, or nitro and R² is hydrogen or methyl, or R¹ and R² together form a methylenedioxy group; R³ is hydroxy, chloro or an esterifying group and Y¹, Y², Y³, Y⁴, Y⁵ and Y⁶ are the same or different groups and each is hydrogen or a fluoro, bromo or chloro, at least one of Y¹, Y², Y³, Y⁴, Y⁵ and Y⁶ being fluoro, bromo or chloro; or a salt of a compound where R³ is hydroxy with an organic or inorganic base.

50 2. A compound as claimed in claim 1 characterised in that R¹ is a methoxy, ethoxy or propoxy group and R² is hydrogen, or R¹ and R² together form a methylenedioxy group.

3. A compound as claimed in claim 1 or claim 2, characterised in that from one to all six of the groups Y¹ to Y⁶ is a fluoro group, the remainder (if any) being hydrogen.

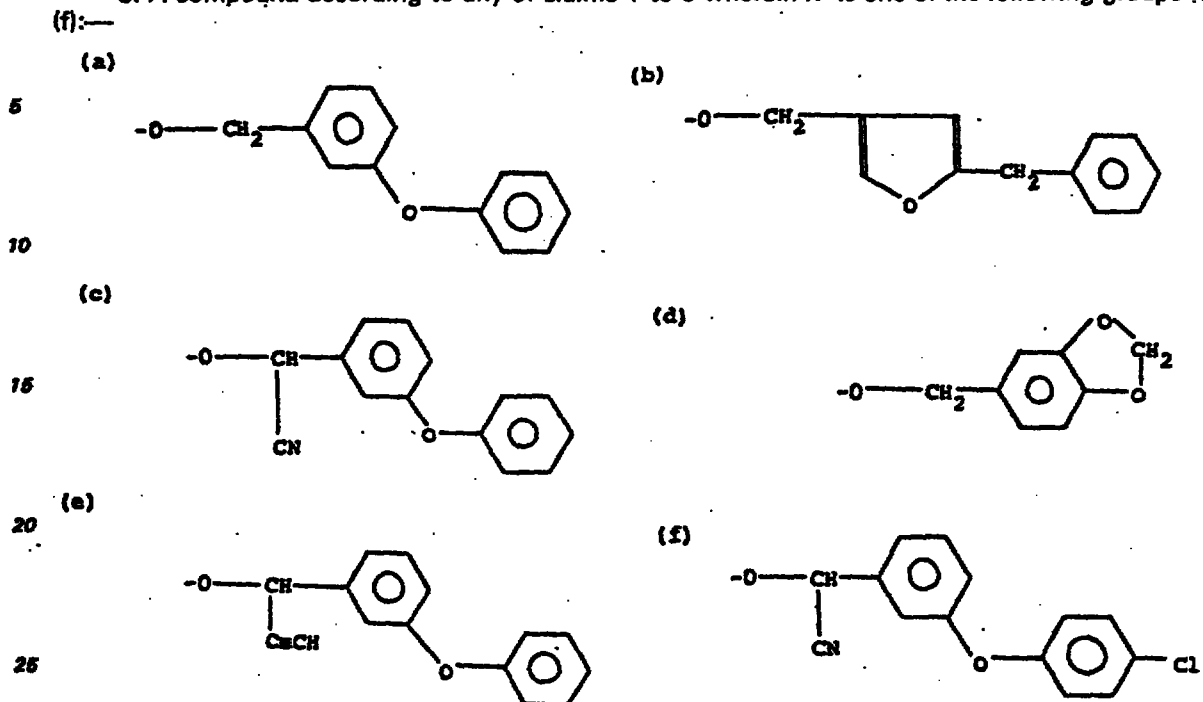
4. A compound as claimed in claim 3, characterised in that Y¹, Y², Y³ and Y⁴ are all fluoro and Y⁵ and Y⁶ are hydrogen.

5. A compound according to any preceding claim characterised in that R¹ is chloro, fluoro, ethoxy or tetrafluoroethoxy and R² is hydrogen or R¹ and R² together form a methylenedioxy group.

6. A compound according to any of claims 1 to 5 characterised in that it is in the (—) form.

7. A compound according to any of claims 1 to 6 characterised in that R³ is alkoxy containing up to 8 carbon atoms.

8. A compound according to any of claims 1 to 6 wherein R^3 is one of the following groups (f):—



9. A compound according to claim 8 in which R^3 is one of the groups a, c or e defined in claim

10. A compound according to claim 8 and which is 3' - phenoxy - benzyl 1 - (3-methylenedioxyphenyl) - 2,2,3,3 - tetrafluorocyclobutane-carboxylate.

11. A compound according to claim 8 and which is α - ethynyl - 3' - phenoxybenzyl 1 - (3-methylenedioxyphenyl) - 2,2,3,3 - tetrafluorocyclobutanecarboxylate.

12. A compound according to claim 8 and which is 3' - phenoxybenzyl 1 - (4 - ethoxyphenyl) - 2,2,3,3 - tetrafluorocyclobutane-carboxylate.

13. A compound according to claim 8 and which is α - cyano - 3' - phenoxybenzyl 1 - (4 - ethoxyphenyl) - 2,2,3,3 - tetrafluorocyclobutanecarboxylate.

14. A compound according to claim 8 and which is α - ethynyl - 3' - phenoxybenzyl 1 - (4 - ethoxyphenyl) - 2,2,3,3 - tetrafluorocyclobutanecarboxylate.

15. An insecticidal or nematocidal composition comprising an inert liquid or solid carrier and an active ingredient characterised in that it contains as an active ingredient a compound according to any of claims 8 to 14.

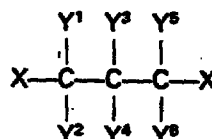
16. An insecticidal or nematocidal composition as claimed in claim 15 characterised in that it additionally contains at least one synergistic or potentiating agent of the class of microsomal inhibitors, preferably a pyrethrin synergist.

17. An insecticidal or nematocidal composition as claimed in claim 16 characterised in that the synergist is 2 - (3,4 - methylenedioxy - phenoxy) - 3,6,9 - trioxaundecane or α [2 - (2 - butoxyethoxy) - ethoxy] - 4,5 - methylenedioxy - 2 - propyltoluene used in an amount of 0.001 to preferably 0.01 to 1, parts by weight per part by weight of the compound according to any of claims 8 to 14.

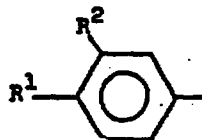
18. A compound according to any of claims 8 to 14 for use as an insecticide.

19. A method for preparing a compound as defined in any of claims 8 to 14 characterised in that the free acid of formula I wherein R^3 is hydroxy, or a reactive derivative or alkyl ester thereof where the alkyl group contains up to 8 carbon atoms, is esterified with an alcohol of the formula R^3H , where R^3 is one of the said groups (a) to (f).

20. A method for preparing a compound as defined in any of claims 1 to 6 wherein R^3 is hydroxy, characterised in that the process comprises reacting a compound of the formula $PhCH_2Z$ with a compound of the formula:—

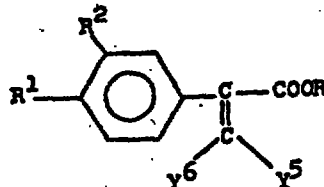


to form a 1-phenylcyclobutane compound and then hydrolysing this to the acid wherein Ph is



X is chloro, bromo or iodo and Z is a group that activates the benzylic methylene and is hydrolysable to a carboxylic group.

21. A method for preparing a compound as defined in claim 7 wherein R^3 is alkoxy containing up to 8 carbon atoms characterised in that it comprises reacting an olefin $Y^1Y^2C=CY^3Y^4$ with a substituted phenylacrylic ester of formula II

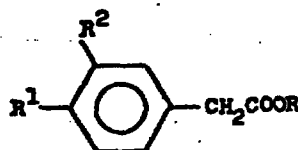


II

wherein R is an alkyl group containing up to 8 carbon atoms and R^1 , R^2 , Y^1 , Y^2 , Y^3 , Y^4 , Y^5 and Y^6 are as defined in claim 1.

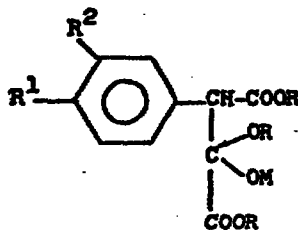
22. A method for preparing a compound as defined in claim 7 wherein R^3 is alkoxy containing up to 8 carbon atoms and wherein $Y^3 = Y^4 = F$ and $Y^1 = Y^2 = Y^5 = Y^6 = H$, characterised in that the method comprises reacting a compound of formula II, stated in claim 21 wherein $Y^5 = Y^6 = H$, with dichlorodifluoroethylene to produce a compound of formula I wherein R^3 is alkoxy containing up to 8 carbon atoms and $Y^3 = Y^4 = F$, $Y^1 = Y^2 = Cl$ and $Y^5 = Y^6 = H$, and hydrogenating this compound to replace the chloro groups by hydrogen.

23. A method as claimed in claim 21 or claim 22 characterised in that the phenylacrylic ester of formula II has $Y^5 = Y^6 = H$ and has been obtained by
(1) condensing the appropriately substituted phenyl acetic ester of formula V



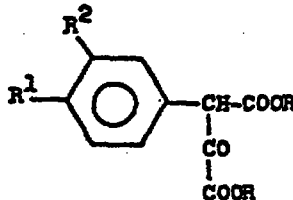
V

with a dialkyl oxalate (wherein the alkyl groups each contain up to 8 carbon atoms) in the presence of a solvent and basic catalyst, to produce a solution of salt of formula IV



IV

(2) acidifying the solution of the salt IV to give the corresponding phenyloxaloacetate III

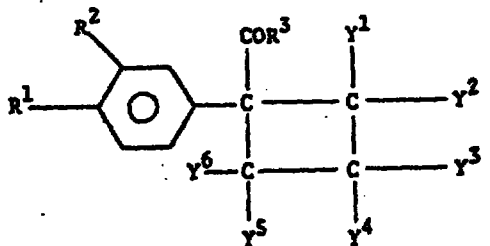


III

(3) reacting the compound III with formaldehyde under alkaline conditions to give the corresponding phenyl hydroxymethyl acetate which is then dehydrated to the ester II; wherein in the above formulae R^1 and R^2 are as defined in claim 1, the groups R are alkyl groups containing up to 8 carbon atoms, which may be the same or different, and M is an alkali metal.

Patentansprüche

1. Verbindung der allgemeinen Formel I:



in welcher R¹ für Wasserstoff oder Methoxy, Äthoxy, Propoxy, Butoxy, Tetrafluoräthoxy, Methylthio, Äthylthio, Propylthio, Fluor, Chlor, Brom, Methyl, Äthyl oder Nitro steht, und R² Wasserstoff oder Methyl bedeutet, oder R¹ und R² gemeinsam eine Methylendioxygruppe bedeuten; R³ für Hydroxy, Chlor oder eine veresternde Gruppe steht, und Y¹, Y², Y³, Y⁴, Y⁵ und Y⁶ für die gleichen oder unterschiedliche Gruppen stehen und jeweils Wasserstoff oder Fluor, Brom oder Chlor bedeuten, wobei mindestens ein Substituent Y¹, Y², Y³, Y⁴, Y⁵ und Y⁶ für Fluor, Brom oder Chlor steht; oder ein Salz der Verbindung, in welcher R³ für Hydroxy steht, mit einer organischen oder anorganischen Base.

2. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß R¹ für eine Methoxy-, Äthoxy- oder Propoxygruppe steht und R² Wasserstoff bedeutet oder R¹ und R² gemeinsam eine Methylendioxygruppe bilden.

3. Verbindung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß eine bis alle 6 der Gruppen Y¹ bis Y⁶ für eine Fluorgruppe steht bzw. stehen, wobei der (gegebenenfalls vorliegende) Rest Wasserstoff ist.

4. Verbindung nach Anspruch 3, dadurch gekennzeichnet, daß Y¹, Y², Y³ und Y⁴ jeweils für Fluor stehen und Y⁵ und Y⁶ Wasserstoff bedeuten.

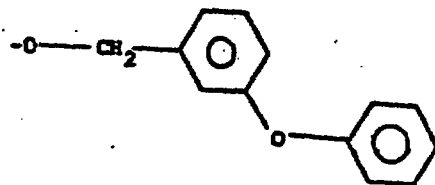
5. Verbindung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß R¹ für Chlor, Fluor, Äthoxy oder Tetrafluoräthoxy steht und R² Wasserstoff bedeutet oder R¹ und R² gemeinsam eine Methylendioxygruppe bilden.

6. Verbindung nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß sie in der (—) Form vorliegt.

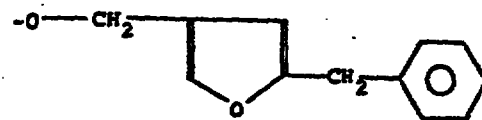
7. Verbindung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß R³ für Alkoxy mit bis zu 8 Kohlenstoffatomen steht.

8. Verbindung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß R³ für eine der folgenden Gruppen (a) bis (f) steht:

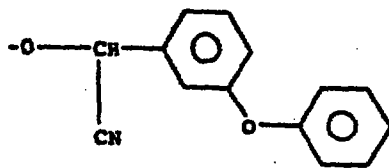
(a)



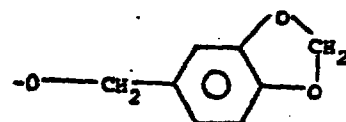
(b)



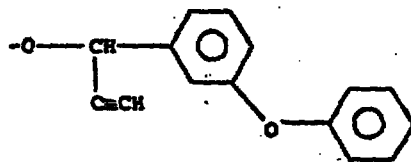
(c)



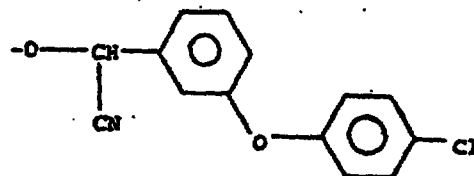
(d)



(e)

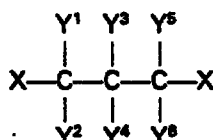


(f)

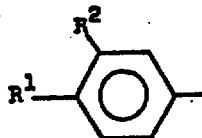


9. Verbindung nach Anspruch 8, dadurch gekennzeichnet, daß R³ für eine der Gruppen a), c) oder e) gemäß Anspruch 8 steht.

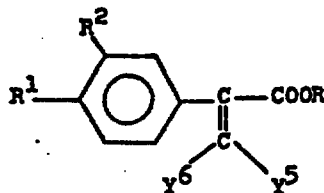
10. Verbindung nach Anspruch 8, nämlich 3' - Phenoxy - benzyl - 1 - (3,4 - methylen-dioxyphenyl) - 2,2,3,3 - tetrafluorocyclobutancarboxylat.
11. Verbindung nach Anspruch 8 nämlich α -Äthynyl - 3' - phenoxybenzyl - 1 - (3,4 - methylenedioxyphenyl) - 2,2,3,3 - tetrafluorocyclobutancarboxylat.
12. Verbindung nach Anspruch 8, nämlich 3' - Phenoxybenzyl - 1 - (4 - äthoxyphenyl) - 2,2,3,3 - tetrafluorocyclobutancarboxylat.
13. Verbindung nach Anspruch 8, nämlich α - Cyan - 3' - phenoxybenzyl - 1 - (4 - äthoxyphenyl) - 2,2,3,3 - tetrafluorocyclobutancarboxylat.
14. Verbindung nach Anspruch 8, nämlich α - Äthynyl - 3' - phenoxybenzyl - 1 - (4 - äthoxyphenyl) - 2,2,3,3 - tetrafluorocyclobutancarboxylat.
15. Insektizides oder nematozides Präparat, enthaltend einen inerten flüssigen oder festen Träger und einen aktiven Bestandteil, dadurch gekennzeichnet, daß es als aktiven Bestandteil eine Verbindung nach einem der Ansprüche 8 bis 14 enthält.
16. Insektizides oder nematozides Präparat nach Anspruch 15, dadurch gekennzeichnet, daß es zusätzlich mindestens ein synergistisches oder potenzierendes Mittel aus der Klasse mikrosomer Oxidaseinhibitoren, vorzugsweise einen Pyrethrinsynergisten, enthält.
17. Insektizides oder nematozides Präparat nach Anspruch 16, dadurch gekennzeichnet, daß der Synergist 2 - (3,4 - Methylendioxy - phenoxy) - 3,6,9 - trioxaundecan oder α - [2 - (2 - Butoxy - äthoxy) - äthoxy] - 4,5 - methylenedioxy - 2 - propyltoluol ist und in einer Menge von 0,001 bis 5, vorzugsweise 0,01 bis 1, Gew. Teilen pro Gew.-Teil Verbindung gemäß einem der Ansprüche 8 bis 14 verwendet wird.
18. Verbindung nach einem der Anspruch 8 bis 14 zur Verwendung als Insektizid.
19. Verfahren zur Herstellung einer Verbindung nach einem der Ansprüche 8 bis 14, dadurch gekennzeichnet, daß die freie Säure der Formel I, in welcher R^3 für Hydroxy steht, oder ein reaktionsfähiges Derivat oder ein Alkylester derselben, in welchem die Alkylgruppe bis zu 8 Kohlenstoffatome enthält, mit einem Alkohol der Formel R^3H , in welcher R^3 für eine der Gruppen (a) bis (f) steht, verestert wird.
20. Verfahren zur Herstellung einer Verbindung nach einem der Ansprüche 1 bis 6, in welcher R^3 für Hydroxy steht, dadurch gekennzeichnet, daß man eine Verbindung der Formel $PhCH_2Z$ mit einer Verbindung der Formel:



unter Bildung einer 1-Phenylcyclobutanverbindung umgesetzt und diese dann zur Säure hydrolysiert, wobei Ph für

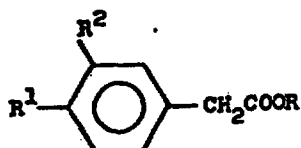


- steht, X Chlor, Brom oder Jod bedeutet, und Z für eine Gruppe steht, die die benzyliche Methylengruppe aktiviert und in eine Carboxylgruppe hydrolysierbar ist.
21. Verfahren zur Herstellung einer Verbindung gemäß Anspruch 7, in welcher R^3 für eine Alkoxygruppe mit bis zu 8 Kohlenstoffatomen steht, dadurch gekennzeichnet, daß man ein Olefin $Y^1Y^2C = CY^3Y^4$ mit einem substituierten Phenylacrylester der Formel II umsetzt:



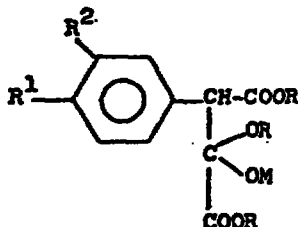
- in welcher R für eine Alkylgruppe mit bis zu 8 Kohlenstoffatomen steht und R^1 , R^2 , Y^1 , Y^2 , Y^3 , Y^4 , Y^5 und Y^6 die in Anspruch 1 angegebene Bedeutung haben.
22. Verfahren zur Herstellung einer Verbindung gemäß Anspruch 7, in welcher R^3 für eine Alkoxygruppe mit bis zu 8 Kohlenstoffatomen steht und $Y^3 = Y^4 = F$ und $Y^1 = Y^2 = Y^5 = Y^6 = H$ sind, dadurch gekennzeichnet, daß man eine Verbindung der Formel II gemäß Anspruch 21, in welcher $Y^5 = Y^6 = H$ ist mit Dichlordifluoräthylen unter Bildung einer Verbindung der Formel I, in welcher R^3 für eine Alkoxygruppe mit bis zu 8 Kohlenstoffatomen steht und $Y^3 = Y^4 = F$, $Y^1 = Y^2 = Cl$ und $Y^5 = Y^6 = H$ sind, umsetzt und diese Verbindung zwecks Austausch der Chlorgruppen durch Wasserstoff hydriert.

23. Verfahren nach Anspruch 21 oder 22, dadurch gekennzeichnet, daß im Phenylacrylester der Formel II $Y^5 = Y^6 = H$ ist und dieser erhalten worden ist, indem man (1) den entsprechend substituierten Phenylessigester der Formel V



V

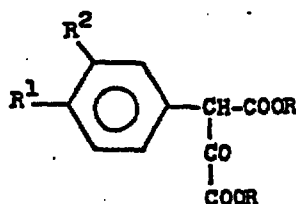
mit einem Dialkyloxalat (in welchem die Alkylgruppen jeweils bis zu 8 Kohlenstoffatom enthalten) in Anwesenheit eines Lösungsmittels und eines basischen Katalysators unter Bildung einer Lösung des Salzes der Formel IV:



IV

kondensiert;

(2) die Lösung des Salzes IV zur Bildung des entsprechenden Phenylxaloacetates III ansäuert:



III

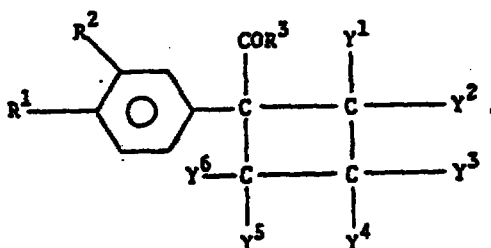
und

(3) die Verbindung III mit Formaldehyd unter alkalischen Bedingungen zur Bildung des entsprechenden Phenylhydroxymethylacetates umsetzt, das dann zum Ester II dehydriert wird;

wobei in den obigen Formeln R^1 und R^2 wie in Anspruch 1 definiert sind, die Gruppen R Alkylgruppen mit bis zu 8 Kohlenstoffatomen sind, die gleich oder verschieden sein können, und M ein Alkalimetall bedeutet.

Revendications

1. Un composé de formule générale I



(I)

dans laquelle R^1 est l'hydrogène, ou un groupe méthoxy, éthoxy, propoxy, butoxy, tétrafluoroéthoxy, méthylthio, éthylthio, propylthio, fluoro, chloro, bromo, méthyle, éthyle, ou nitro, et R^2 est l'hydrogène ou un groupe méthyle, ou bien R^1 et R^2 forment ensemble un groupe méthylènedioxy, R^3 est un groupe hydroxy chloro ou un groupe estérifiant et Y^1, Y^2, Y^3, Y^4, Y^5 et Y^6 sont des groupes identiques ou différents représentant chacun l'hydrogène ou un groupe fluoro, bromo ou chloro, au moins l'un des groupes Y^1, Y^2, Y^3, Y^4, Y^5 et Y^6 étant un groupe fluoro, bromo ou chloro; ou un sel d'un composé dans lequel R^3 est un groupe hydroxy avec une base minérale ou organique.

2. Un composé selon la revendication 1, caractérisé en ce que R^1 est un groupe méthoxy, éthoxy ou propoxy et R^2 est l'hydrogène, ou R^1 et R^2 forment ensemble un groupe méthylènedioxy.

3. Un composé selon la revendication 1 ou 2, caractérisé en ce que de un à six des groupes Y^1 à Y^6 sont des groupes fluoro, les autres (s'il y en a) étant de l'hydrogène.

4. Un composé selon la revendication 3, caractérisé en ce que Y^1, Y^2, Y^3 et Y^4 sont tous des groupes fluoro et Y^5 et Y^6 sont de l'hydrogène.

5. Un composé selon l'une quelconque des revendications précédentes, caractérisé en ce que R^1

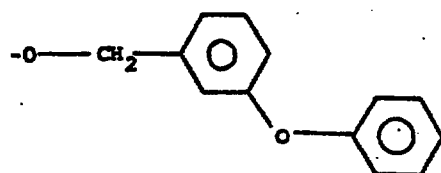
est un groupe chloro, fluoro, éthoxy ou tétrafluoroéthoxy et R² est l'hydrogène ou R¹ et R² forment ensemble un groupe méthylènedioxy.

6. Un composé selon l'une quelconque des revendications 1 à 5, caractérisé en ce qu'il est sous la forme (-).

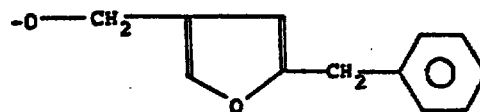
7. Un composé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que R³ est un groupe alcoxy contenant jusqu'à 8 atomes de carbone.

8. Un composé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que R³ est choisi parmi les groupes (a) à (f) suivants:

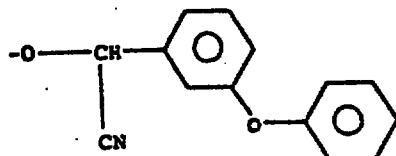
(a)



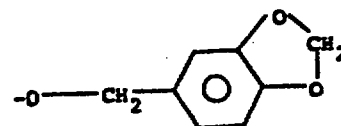
(b)



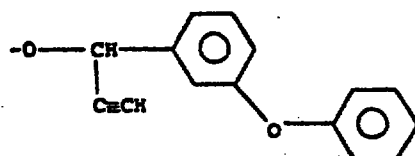
(c)



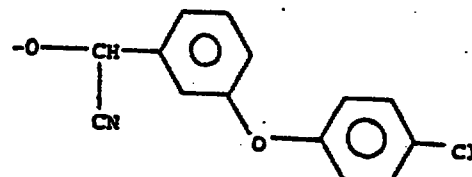
(d)



(e)



(f)



9. Un composé selon la revendication 8, caractérisé en ce que R³ est l'un des groupes (a), (c) ou (e) défini dans la revendication 8.

10. Un composé selon la revendication 8 qui est le 1 - (3,4 - méthylènedioxyphényl) - 2,2,3,3 - tétrafluorocyclobutanecarboxylate de 3'-phénoxybenzyle.

11. Un composé selon la revendication 8 qui est le 1 - (3,4 - méthylènedioxyphényl) - 2,2,3,3 - tétrafluorocyclobutane - carboxylate de α - éthyne - 3' - phénoxybenzyle.

12. Un composé selon la revendication 8 qui est le 1 - (4 - éthoxyphényl) - 2,2,3,3 - tétrafluorocyclobutane - carboxylate de 3'-phénoxybenzyle.

13. Un composé selon la revendication 8 qui est le 1 - (4 - éthoxyphényl) - 2,2,3,3 - tétrafluorocyclobutane - carboxylate de α - cyano - 3' - phénoxybenzyle.

14. Un composé selon la revendication 8 qui est le 1 - (4 - éthoxyphényl) - 2,2,3,3 - tétrafluorocyclobutane - carboxylate de α - éthyne - 3' - phénoxybenzyle.

15. Une composition insecticide ou nématocide comprenant un véhicule liquide ou solide inerte et un ingrédient actif, caractérisée en ce qu'elle contient comme ingrédient actif un composé selon l'une quelconque des revendications 8 à 14.

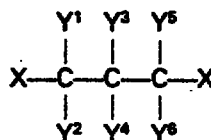
16. Une composition insecticide ou nématocide selon la revendication 15, caractérisée en ce qu'elle contient en outre un agent produisant un effet de synergie ou de potentialisation choisi parmi la classe des inhibiteurs de la microsomal oxidase, de préférence un agent produisant un effet de synergie de la classe de pyrèthrines.

17. Une composition insecticide ou nématocide selon la revendication 16, caractérisée en ce que l'agent produisant l'effet de synergie est le 2 - (3,4 - méthylènedioxyphénoxy) - 3,6,9 - trioxaundécane ou le [2 - (2 - butoxyéthoxy) - éthoxy] - 4,5 - méthylènedioxy - 2 - propyltoluène utilisé à raison de 0,001 à 5, et de préférence de 0,01 à 1, parties en poids par partie en poids du composé selon l'une quelconque des revendications 8 à 14.

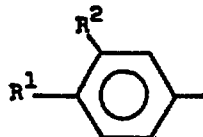
18. Un composé selon l'une quelconque des revendications 8 à 14 utilisé comme insecticide.

19. Un procédé de préparation d'un composé tel que défini à l'une quelconque des revendications 8 à 14, caractérisé en ce que l'acide libre de formule I dans lequel R³ est un groupe hydroxy ou un dérivé réactif, ou un ester alkylique de ce composé dans lequel le groupe alkyle contient jusqu'à 8 atomes de carbone, est estérifié avec un alcool de formule R³H, dans laquelle R³ est un des groupes (a) à (f).

20. Un procédé de préparation d'un composé tel que défini dans l'une des revendications 1 à 6, dans lequel R^3 est un groupe hydroxy, caractérisé en ce que le procédé consiste à faire réagir un composé de formule PhCH_2Z avec un composé de formule

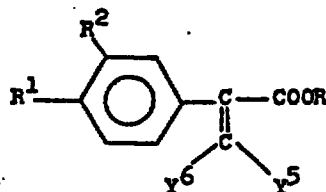


pour former un dérivé de 1-phénylcyclobutane et ensuite à hydrolyser ce dérivé en l'acide dans lequel Ph est un groupe



X est un groupe chloro, bromo ou iodo et Z est un groupe qui active le groupe méthylène benzylique et qui est hydrolysable en un groupe carboxylique.

21. Un procédé de préparation d'un nouveau composé tel que défini dans la revendication 7, dans lequel R^3 est un groupe alcoxy contenant jusqu'à 8 atomes de carbone, caractérisé en ce qu'il consiste à faire réagir une oléfine $\text{Y}^1\text{Y}^2\text{C} = \text{CY}^3\text{Y}^4$ avec un ester phénylacrylique substitué de formule II

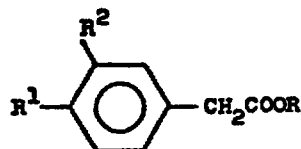


(II)

dans laquelle R est un groupe alkyle contenant jusqu'à 8 atomes de carbone et R^1 , R^2 , Y^1 , Y^2 , Y^3 , Y^4 , Y^5 et Y^6 sont tels que définis dans la revendication 1.

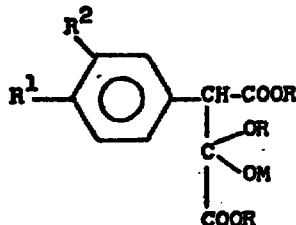
22. Un procédé de préparation d'un nouveau composé tel que défini à la revendication 7 dans lequel R^3 est un groupe alcoxy contenant jusqu'à 8 atomes de carbone et $Y^3 = Y^4 = \text{F}$ et $Y^1 = Y^2 = Y^5 = Y^6 = \text{H}$, caractérisé en ce que le procédé consiste à faire réagir un composé de formule II tel que défini à la revendication 21, dans laquelle $Y^5 = Y^6 = \text{H}$ avec le dichlorodifluoroéthylène pour former un composé de formule I dans laquelle R^3 est un groupe alcoxy contenant jusqu'à 8 atomes de carbone et $Y^3 = Y^4 = \text{F}$, $Y^1 = Y^2 = \text{Cl}$ et $Y^5 = Y^6 = \text{H}$, et à hydrogéner ce composé pour remplacer les groupes chloro par de l'hydrogène.

23. Un procédé selon la revendication 21 ou 22, caractérisé en ce que l'ester phénylacrylique de formule II dans laquelle $Y^5 = Y^6 = \text{H}$ a été obtenu par
(1) condensation de l'ester phénylacétique convenablement substitué de formule V



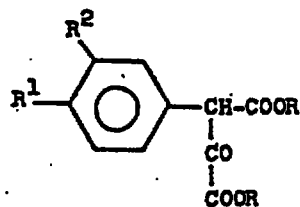
(V)

avec un oxalate de dialcoyle (dans lequel chacun des groupes alkyle contient jusqu'à 8 atomes de carbone) en présence d'un solvant et d'un catalyseur basique pour former une solution d'un sel de formule IV



(IV)

(2) acidification de la solution du sel IV pour former le phényloxaloacétate III correspondant



10 (3) réaction de composé III avec le formaldéhyde dans des conditions alcalines pour former le phénylhydroxyméthylacétate qui est ensuite déshydraté en l'ester de formule II;
 dans les formules ci-dessus R¹ et R² étant tels que définis dans la revendication 1, les groupes R étant
 des groupes alcoyle contenant jusqu'à 8 atomes de carbone qui peuvent être identiques ou différents et
 15 M est un métal alcalin.

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