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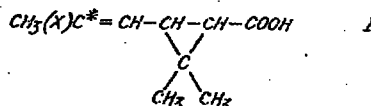
(54) 3-SUBSTITUTED-2,2-DIMETHYL-CYCLOPROPANE
CARBOXYLIC ACID ESTERS, THEIR PREPARATION
AND THEIR USE IN PESTICIDAL COMPOSITIONS

(71) We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, a British Corporation established by statute of Kingsgate House, 66—74 Victoria Street, London S.W.1, England, 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 insecticides and more particularly to synthetic insecticides of the pyrethrin type, to their preparation, to compositions containing them and to the insecticidal use of the compounds and compositions.

For many years, research has been pursued in the field of synthetic analogues of the pyrethrins to discover synthetic substitutes having properties superior to those of the natural products. Ideally, synthetic analogues of the naturally occurring pyrethrins should compare well with or be superior to the natural products as regards level of toxicity to insects and mammals, insecticidal spectrum and knock down properties and, in addition, should offer ease of manufacture.

Since the discovery that the naturally occurring pyrethrins were esters of certain substituted cyclopropane carboxylic acids and substituted cyclopentenolones, the search for synthetic analogues concentrated initially on modifying the "alcohol" part of the ester molecule and later on modifying the "acid" part of the ester molecule or, in some cases, modifying both parts of the ester molecule. The naturally occurring esters are esters of chrysanthemic or pyrethric acids of the formula:

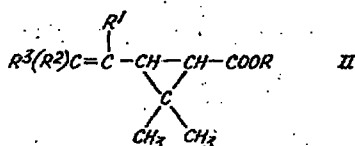


where X represents a methyl group (chrysanthemic acid) or a carbomethoxy group

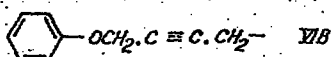
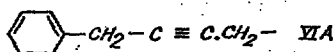
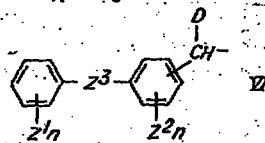
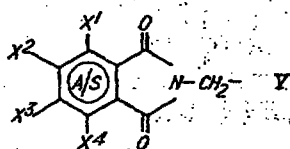
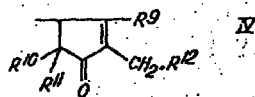
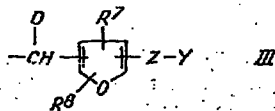
(pyrethric acid). In these acids, the substituents at the asterisked carbon atom are believed to be involved in the detoxification of the pyrethrin insecticides in the insect.

We have now found that a high level of insecticidal activity and a particularly valuable combination of toxicity and knock down properties can be obtained in esters of 2,2 - dimethyl - - alkenyl cyclopropane carboxylic acid where the substitution on the 3-alkenyl side chain differs from that of all previously known pyrethrin-like ethers.

Accordingly, the present invention provides esters of the general formula:



wherein R^1 represents hydrogen or a methyl group; R^2 represents hydrogen or a halogeno or alkyl group; R^3 represents hydrogen or a halogeno, or carbalkoxy group which contains at least 2 carbon atoms in the alkoxy residue when R^2 represents methyl; with the proviso that (a) R^2 and R^3 each represent hydrogen only when R^1 represents methyl and (b) when R^1 and R^3 represent hydrogen, R^2 represents alkyl, that alkyl group contains at least two carbon atoms; and R represents a group of formula:



wherein Z represents O, S, CH_2 or CO, Y represents hydrogen or an alkyl, alkenyl or alkynyl group or an aryl or furyl group which is unsubstituted or substituted in the ring by one or more alkyl, alkenyl, alkoxy or halogeno groups, R^7 and R^8 , which may be the same or different, each represent hydrogen or an alkyl, or alkenyl group,

R^9 represents hydrogen or a methyl group,

R^{10} and R^{11} , which may be the same or different, each represent hydrogen or an alkyl group,

R^{12} represents an organic radical having carbon-carbon unsaturation in a position α to the CH_2 group to which R^{12} is attached,

(A/S) indicates an aromatic ring or a dihydro or tetrahydro analogue thereof,

X^1 , X^2 , X^3 and X^4 , which may be the same or different, each represent hydrogen, chlorine or a methyl group,

Z^1 represents $-CH_2-$ or $-O-$ or $-S-$ or $-CO-$, D represents H, CN or $-C \equiv CH$, Z^1 and Z^2 , which may be the same or different, each represent chlorine or a methyl group and each n, which may be the same or different, is 0, 1 or 2, with the proviso that R does not represent an allethronyl group when R^1 represents hydrogen, R^2 and R^3 each represent chlorine and the compound is racemic.

The esters of the present invention where R represents a group of formula III, IV, V, VI, VIA or VIB are insecticidal esters having a valuable combination of toxicity and knock down properties. The level of insecticidal activity of the new compounds is surprisingly high, ($\pm$) - α - cyano - 3 - phenoxy benzyl - (+) - *cis*-[1R,3S] - 2,2 - dimethyl - 3 - (2,2 - dibromovinyl)cyclopropane carboxylate being 10 and 11 times respectively more toxic to houseflies and mustard beetles than 5-benzyl - 3 - furylmethyl - (+) - *trans* chrysanthemate while many other esters of the invention have toxicities 2—5 times that of the chrysanthemate.

The esters of formula II where R represents alkyl are useful intermediates in the production of the insecticidal esters e.g. by transesterification. Most of these alkyl esters, together with the corresponding free acids, salts and acid halides are new compounds and the new alkyl esters, free acids, salts and acid halides where at least one of R² and R³ represents halogen are claimed in divisional application Nos. As will be discussed in more detail below, the new alkyl esters can be prepared in that form by a Wittig synthesis and it is not necessary to convert the alkyl ester into the free carboxylic acid in order to produce the insecticidal esters of the invention. However, if desired the alkyl esters can be converted into the free carboxylic acid, e.g. by hydrolysing the ester to give a salt and subsequently acidifying the salt.

The esters of formula II where R represents alkyl and R³=carboalkoxy are useful intermediates in the production of the insecticidal esters which can be converted by acid catalysis, e.g. using toluene - 4 - sulphonic acid in benzene, to the corresponding free carboxylic acid without affecting the carboalkoxy group R³. As will be discussed in more detail below, the new alkyl esters are prepared in that form by a Wittig synthesis and it is necessary to convert the alkyl ester into the free carboxylic acid in order to produce the insecticidal esters of the invention. This is best achieved selectively utilising a *t*-butyl ester (R=*t*-butyl). However, if desired, a *t*-butyl or other alkyl ester can be converted into the free carboxylic acid, by partial saponification but it is difficult to prevent saponification of the carboalkoxy group R³ at the same time.

The insecticidal esters of the present invention may be regarded structurally as esters of a 3-substituted-2,2-dimethylcyclopropane carboxylic acid and an alcohol e.g. a benzyl alcohol, a furylmethyl alcohol, a cyclopentenolone or an α -cyano, or α -ethynyl benzyl or α -cyano- or α -ethynyl-furylmethyl-alcohol. While the esters may be conveniently described structurally in these terms, it will be appreciated and explained in more detail below, that the esters can be prepared by methods other than esterifying the acid with the alcohol and, in practice, normally are.

So far as the various values of R² and R³ are concerned, it is preferred that when these groups include alkyl or alkoxy groups, the groups contain up to 6 carbon atoms, and, more particularly, up to 3 carbon atoms, methyl, ethyl, propyl, methoxy, ethoxy, and propoxy, being of particular interest. When R² and/or R³ represents a halogeno group, it is preferably fluorine, chlorine or bromine. When R² and R³ each represent halogeno, they are preferably, but not necessarily the same halogen.

The esters of the present invention fall into various sub-classes structurally, depending primarily upon the nature of substituent R² and R³. One sub-class of particular interest are those compounds where R¹ and R³ each represent hydrogen and R² represents an alkyl group of at least two carbon atoms. We have now found that in this sub-class the highest toxicity to houseflies and mustard beetles of 5-benzyl-3-furylmethyl esters of 3- β -alkylvinyl-2,2-dimethylcyclopropane carboxylic acid is shown when the alkyl group is ethyl.

Further sub-classes of particular interest are those esters where R¹ and R³ each are hydrogen and R² is chlorine or bromine and those compounds where R¹ is methyl and R³ is hydrogen, and R² is hydrogen or an alkyl group containing up to 6 carbon atoms such as methyl, ethyl or propyl.

Another sub-class of particular interest are those compounds where R³ represents a carboalkoxy group (containing at least 2 carbon atoms in the alkoxy residue when R² represents methyl), R² represents hydrogen or an alkyl group and R¹ represents hydrogen. This sub-class includes compounds where R² represents hydrogen and R³ represents a carboalkoxy group. These esters are esters of a demethyl pyrethric acid analogue which is devoid of the methyl substituent on the β carbon atom of the 3-substituent. A further sub-class of considerable importance are those esters where R² represents methyl and R³ represents a carboalkoxy group, where the alkoxy residue contains at least two carbon atoms. These esters are esters of pyrethric acid analogues which do not contain the carbomethoxy substituent on the β carbon atom of the 3-substituent.

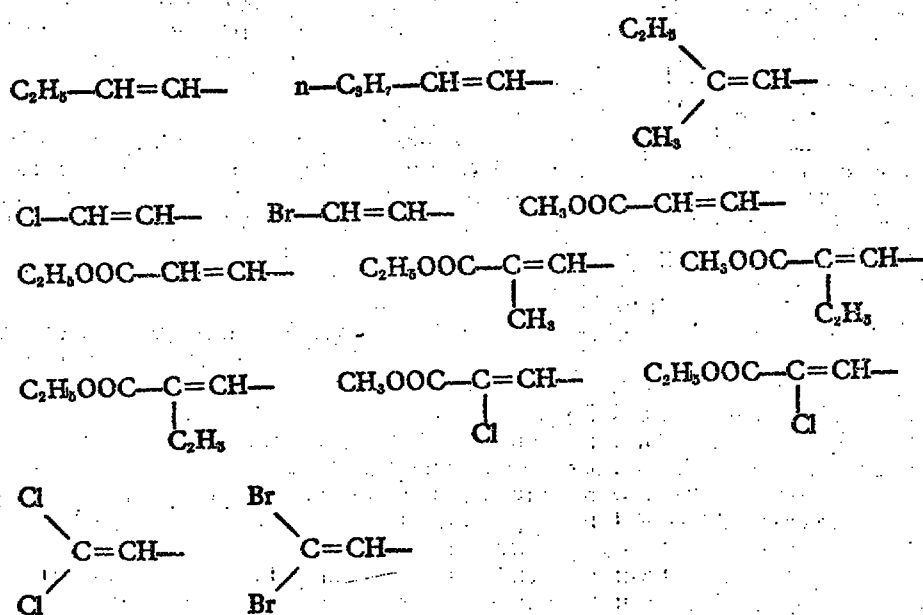
Further sub-classes of particular interest are those esters where R² represents an

alkyl group of at least two carbon atoms; again these esters are esters of a pyrethric acid homologue which does not contain the methyl substituent on the asterisked carbon atom of formula I. In these esters, R³ may represent the carbomethoxy group (which is present in pyrethric acid) or a higher homologue thereof.

The most active of the insecticidal esters of the invention are those where R² and R³ each represent a halogeno group, and R¹ preferably represents hydrogen, the 5-benzyl-3-furylmethyl esters of the various isomeric 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylic acids being up to 2½ times more toxic to houseflies than the corresponding ester of (+)-*trans*-chrysanthemic acid, itself 50 times more toxic to normal houseflies than natural pyrethrin I. Esters of these acids with 3-phenoxybenzyl- and α-cyano-3-phenoxybenzyl alcohol give esters which are 2 to 11 times more toxic than 5-benzyl-3-furylmethyl (+)-*trans*-chrysanthemate. Esters of these 3-dihalovinyl acids also of particular value because of their greater light stability than the corresponding chrysanthemates.

A further halogenated sub-class of interest are those esters where R¹ represents hydrogen, R² represents halogeno and R³ represents carboalkoxy. The acid residue in these esters are analogues of pyrethric acid where the methyl substituent on the β-carbon atom of the 3-substituent is replaced by the halogeno and homologues of these acids where the carbomethoxy group is replaced by a carboalkoxy group containing at least 3 carbon atoms. The halogen is preferably chlorine or bromine and the carboalkoxy group is preferably carbo-methoxy, -ethoxy or -*n*-propoxy.

Preferred esters of the present invention include those which are structurally esters of a 2,2-dimethyl-substituted cyclopropane carboxylic acid where the 3-substituent is:



When the ester is one structurally derived from a furylmethyl alcohol it is preferred that the furylmethyl alcohol be one of the 3-furylmethyl alcohols described in British Patent Specification No. 1,168,798. In the furylmethyl alcohols, and particularly in the 3-furylmethyl alcohols, it is preferred that R¹ and R³ each represent hydrogen or groups containing up to 4 carbon atoms, particularly a methyl group and that Y represents a phenyl group which is unsubstituted or substituted in the ring by a group containing up to 4 carbon atoms, e.g. methyl or methoxy, or by chlorine, and Z=CH₂, O or CO— and D=H. Analogues of these compounds where Z=S and D=CN or C≡CH can also be used. Other compounds of interest are those where Y represents a hydrogen atom, an alkyl group containing up to 4 carbon atoms, an alkenyl group containing up to 4 carbon atoms, e.g. vinyl, an alkadienyl group containing up to 4 carbon atoms or an alkynyl group e.g. propargyl or a furyl group.

Specific alcohols of this category, from which the esters of the invention are structurally derivable, include 5-benzyl-3-furylmethyl alcohol, 5-benzyl-2-methyl-3-furylmethyl alcohol, 5-benzylfurfuryl alcohol, 4-benzyl-5-methyl-furfuryl alcohol, 5-*p*-xylyl-furfuryl alcohol, 2,4,5-trimethyl-3-furylmethyl alcohol, 4,5-dimethyl-furfuryl alcohol, 5-phenoxy- and 5-benzoyl-3-furylmethyl alcohol and α-cyano and α-ethynyl-5-benzyl-5-benzoyl and 5-phenoxy-3-furylmethyl alcohol.

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The cyclopentenolones from which the esters of the invention are structurally derivable are those unsubstituted in the 3-position or those substituted in the 3-position by a methyl group, ($R^9=H$ or CH_3).

The cyclopentenolones unsubstituted in the 3-position are described in British Patent Specification No. 1,305,025. Some of these alcohols are the 3-demethyl analogues of the alcohols from which the naturally occurring pyrethrins are derived. In the present invention, it is preferred that R^{10} and R^{11} each represent hydrogen, methyl or ethyl and R^{12} represents an aryl group such as a phenyl group or a phenyl group substituted by a halogeno or alkyl or alkoxy substituent, of 1 to 4 carbon atoms, for example tolyl, xylyl, *p*-chlorophenyl or *p*-methoxyphenyl. R^{12} may also represent a 2- or 3-furyl group or an alkenyl group such as a vinyl, prop-1-enyl or buta-1,3-dienyl group.

When the esters of the invention are structurally derivable from the cyclopentenolones which are substituted in the 3-position by the methyl group, ($R^9=methyl$), the esters may be derived from allethrolone ($R^{10}=R^{11}=H$, $R^{12}=vinyl$), pyrethrolone ($R^{10}=R^{11}=H$, $R^{12}=buta-1,3-dienyl$), cinerolone ($R^{10}=R^{11}=H$, $R^{12}=prop-1-enyl$), jasmolone ($R^{10}=R^{11}=H$, $R^{12}=but-1-enyl$) or furethrolone ($R^{10}=R^{11}=H$, $R^{12}=2-furyl$).

When the esters of the invention are phthalimidomethyl esters where R is of formula V, they may be phthalimido, dihydrophthalimido or tetrahydrophthalimidomethyl esters where the phthalimido, dihydrophthalimido or tetrahydrophthalimido residue is one described in British Patent Specification Nos. 985,006, 1,052,119 or 1,058,309. 3,4,5,6-Tetrahydrophthalimido-methyl esters are of particular interest.

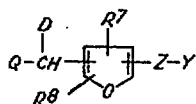
When the esters of the invention are those where R is of formula VI, it is preferred that they be 3-benzylbenzyl esters, 3-benzoylbenzyl esters or 3-phenoxybenzyl esters although each of the rings may be substituted by up to 3 chloro and/or methyl groups. Other esters of particular interest where R is of formula VI are those where Z represents O or CH_2 and D represents $-CN$ or $-C\equiv CH$, e.g. esters of α -cyano- or α -ethynyl-3-phenoxybenzyl alcohol and of α -cyano- or α -ethynyl-3-benzyl- and 3-benzoylbenzyl alcohols.

Esters of the present invention where R^1 , R^2 and R^3 represent the combinations specifically mentioned above and D represents $-CN$ or $-C\equiv CH$ represent a group of esters of particular interest.

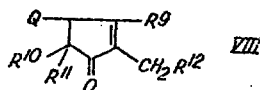
The compounds of the present invention exhibit geometrical and optical isomerism and consequently may be prepared in optically active forms which may subsequently be mixed together or as racemic mixtures which may subsequently be resolved into optically active forms. In addition, optically active forms or racemic mixtures can be separated into the individual geometrical isomers. In addition to the geometrical isomerism that results from the configuration of the substituents on the cyclopropane ring with respect to one another and the ring, there is also the possibility of geometrical isomerism in the side chain on position 3 when R^1 , R^2 and R^3 are such that the unsaturated side-chain is unsymmetrically substituted. In the α -cyano- and α -ethynyl compounds ($D=CN$ or $C\equiv CH$), there is a further possibility of optical isomerism and the compounds envisaged include esters of both the racemic mixture and of the separate isomers resulting from the asymmetry at the carbon atom bearing the D group. The various optical and geometrical isomers of the esters of the invention usually have different insecticidal toxicities and knock down potency.

The compounds of the invention having the hydrogen atoms on the 1 and 3 positions of the cyclopropane ring in the *trans*-relationship to one another are stereo analogues of (+)-*trans*-chrysanthemic acid and for this reason represent a preferred class of compounds of the invention but the present invention also includes compounds where the two hydrogen atoms in question are in the *cis*-relationship. Thus, highly active esters are derived from (+)-*trans* and (+)-*cis*-acids but ($\pm$)-*trans*, ($\pm$)-*cis*, and ($\pm$)-*cis-trans* isomers are also of interest.

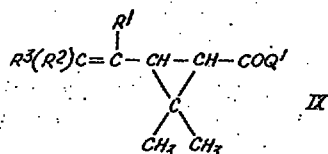
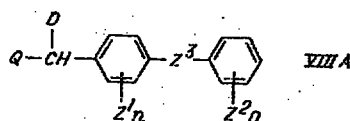
The insecticidal esters of the present invention may be prepared by esterification involving the reaction of an alcohol or derivative thereof formula R—Q e.g. of formula VII, VIII, or VIIIA, and a cyclopropane carboxylic acid or derivative thereof of formula IX,



VII



VIII

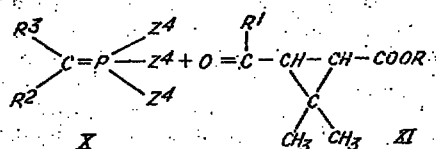


where Q and COQ¹ are functional groups or atoms which will react together to form an ester linkage and R, R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹² and D, Z, Z¹, Z², Z³, Y and n are as defined above.

It is usually convenient in practice either to react the acid or acid halide with the alcohol (COQ¹=COOH or CO—halide and Q=OH) or to react a halogeno compound (Q—halogen) with a salt of the carboxylic acid (COQ¹=COO[⊖]M[⊕] where M is, for example, a silver or triethylammonium cation).

For reasons which will shortly be described, reactant IX normally becomes available initially in the form of a lower alkyl ester, (COQ¹=COO alkyl) where the alkyl group contains 1 to 6 carbon atoms and consequently, a particularly convenient way of preparing the insecticidal esters of the invention, except where R³ is carboalkoxy, is to subject the alkyl ester of formula IX to transesterification using an alcohol ROH, e.g. in the presence of a basic catalyst. When the alkyl ester contains a base sensitive group, e.g. R³=carboalkoxy, base catalysed transesterification is undesirable and can be avoided by preparing a *t*-butyl ester which can be converted into the free acid by acid catalysed decomposition and the free carboxylic group esterified directly or *via* a salt or halide.

The esters of the present invention can also be prepared by reaction between a phosphorane or ylide of formula X and an ester of 2,2-dimethyl cyclopropane carboxylic acid substituted at the 3-position by an acetyl group or an aldehyde group of formula XI:



In formulae X and XI R¹, R², R³ are as defined above and R is a group as defined above which will not interfere in the Wittig reaction and Z⁴, which in principle can represent any organic radical, will normally be a phenyl radical since the stability of the trisubstituted phosphorus oxide which is formed as the by-product in the reaction is particularly high and this favours completion of the reaction between the phosphorane X and the aldehyde or ketone XI.

Esters of the present invention where R¹ represents hydrogen can be prepared by reaction with an aldehyde of formula XI while esters of the invention where R¹ represents methyl can be prepared by reaction of a 3-acetyl compound of formula XI. The phosphorane X and aldehyde or ketone XI are preferably reacted in substantially equimolar proportions, conveniently in the solvent in which the phosphorane itself has been prepared. As will be discussed in more detail below, this may be an aromatic hydrocarbon such as benzene or a polar solvent such as dimethyl sulphoxide or a chlorinated hydrocarbon such as dichloromethane. The product can be improved if reaction is carried out in an inert atmosphere e.g. under nitrogen. The reaction between the phosphorane and aldehyde or ketone is normally quite rapid and the desired ester can be recovered from the reaction mixture after a reaction time of less than 1 hour although reaction times of up to 24 hours have been used. The desired ester can be recovered from the reaction product by solvent extraction e.g. with diethyl ether or petroleum ether.

The phosphorane of formula X where neither R² nor R³ represent halogen can be prepared from the corresponding phosphonium salt which in turn can be prepared by reacting the appropriately substituted methyl halide with a triorganophosphine in accordance with the following reaction scheme:

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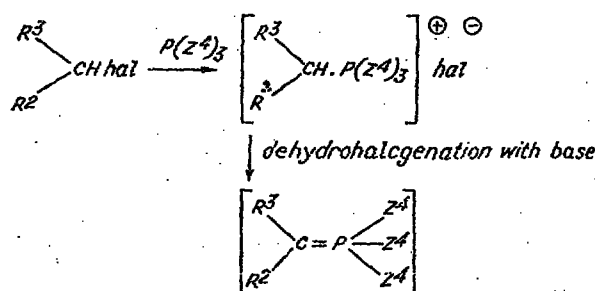
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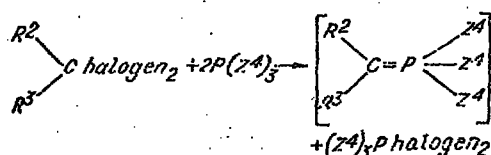
The flexibility of the present synthetic method results from the fact that the initial starting material is the substituted methyl halide $R^3(R^2)CH\ hal$ and the availability of whole series of such substituted halides permits the production of whole series of 2,2-dimethyl cyclopropane carboxylic acids which are substituted in the 3-position by various groups which have previously been difficult or impossible to prepare. In the above-mentioned synthesis of the phosphorane, it is convenient to start with a substituted methyl bromide which is reacted with triphenylphosphine to give the corresponding triphenylphosphonium bromide and subsequently converting the phosphonium salt to the phosphorane or ylide which can be designated by the formula given above. The conversion of the phosphonium salt to the phosphorane can be brought about by treating the phosphonium salt with an alkali metal amide or alkali metal methyl sulphiny methide ($\ominus CH_2 \cdot SO \cdot CH_3 M^+$). For example, sodamide can be prepared by reacting sodium in liquid ammonia and the reaction carried out in the presence of the excess ammonia as the liquid medium. At the end of the reaction, the liquid ammonia can be allowed to evaporate and the phosphorane taken up into an organic solvent such as benzene and the subsequent reaction with aldehyde or ketone XI carried out in this organic solvent. Alternatively, dimethyl sulphoxide can be reacted with sodium hydride to give sodium methyl sulphiny methide and the production of the phosphonium salt carried out using this reagent and, following formation of the phosphorane, the subsequent reaction with the aldehyde or ketone XI can be carried out in the same reaction medium.

When $R^3 = \text{carboalkoxy}$, the conversion of the phosphonium salt to the phosphorane can be brought about by treating the phosphonium salt with an alkali metal amide in liquid ammonia or in aqueous alkali metal hydroxide solution, e.g. 50% NaOH. The liberated phosphorane can be filtered from the solution and subsequently reacted with the aldehyde XI in a suitable solvent e.g. CH_2Cl_2 .

Phosphoranes where R^3 represents carboalkoxy and R^2 represents hydrogen or methyl can be prepared by the above described procedures using a haloacetate or α -halopropionate alkyl ester as the substituted methyl halide but this synthesis is not entirely satisfactory for the preparation of phosphoranes of this type where R^2 represents an alkyl group of 2 or more carbon atoms. For such higher homologues, a phosphorane where R^3 represents hydrogen and R^2 represents the desired alkyl group is first prepared as an intermediate by the procedures described above starting from an alkyl halide of at least 3 carbon atoms and this intermediate phosphorane is then reacted with the appropriate alkyl chloroformate ester to introduce the desired carboalkoxy group.

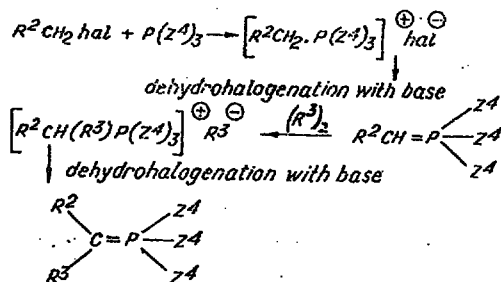
Phosphoranes where R^2 and/or R^3 represent halogen can be prepared by simple modifications of the above described synthesis.

When R^2 and R^3 each represent halogen, a carbon tetrahalide can be used in place of the substituted methyl halide and the reaction proceeds in accordance with the equation:



the dehydrohalogenation of the quaternary phosphonium halide proceeding spontaneously.

Halogenated phosphoranes can also be prepared by halogenating an unhalogenated phosphorane, itself obtained by the above described procedures in accordance with the following reaction scheme:—



where hal=halogen, R^3 =halogen and R^2 is as defined above.

We have found that it is desirable that the carboxyl group in the aldehyde or ketone reactant XI be esterified as a lower alkyl ester (i.e. a C_1 — C_6 alkyl ester) in order to achieve the most satisfactory results in the reaction with the phosphorane X. This means that the alkyl esters are produced directly and, since it is possible to convert these alkyl esters into the insecticidal esters of the invention, except those containing a base sensitive group, e.g. R^3 =carboalkoxy, by a simple base catalysed transesterification reaction, it is not necessary to convert the alkyl esters into the corresponding acid in order to produce the insecticidal esters. However, indirect conversion of the alkyl esters to the insecticidal esters is possible in accordance with the present invention and, when operating in accordance with this embodiment, the carboalkoxy group in the ester of formula II can be converted by conventional hydrolysis into the corresponding free carboxylic acid group going, *via* the alkali metal or other salt for instance, and this carboxylic acid can be directly esterified as described above or alternatively can be converted first into an acid halide e.g. the chloride and this acid halide converted into an ester by reaction with an appropriate alcohol of formula ROH as described above.

In the case where R is a *t*-butyl group, the alkyl ester can be converted into the free acid by heating with a small amount of toluene-4-sulphonic acid. This reaction can be carried out in benzene and the resulting carboxylic acid converted to the acid chloride in the benzene solution without isolation.

In the synthetic methods described so far, alkyl esters are prepared by a Wittig reaction between a phosphorane X and an alkyl ester of a carbonyl compound XI and the resulting alkyl ester converted to an insecticidal ester by transesterification or *via* the free acid and acid chloride which is subsequently reesterified e.g. with 5-benzyl-3-furylmethyl alcohol. It is usually most convenient to operate in this manner but is not essential to do so and a practical alternative is to produce the insecticidal ester directly by reacting the phosphorane X with a carbonyl compound of formula XI where R represents a group of formula III, IV, V, VI, VIA or VIB as defined above.

Such carbonyl compounds of formula XI may be prepared by the synthetic methods described above but converting the group R from an alkyl group to a group of formula III, IV, V, VI, VIA or VIB before the Wittig reaction instead of after the Wittig reaction as described above.

Carbonyl compounds of formula IX can be prepared by ozonolysis of the corresponding ester of chrysanthemic acid, when oxygenation of the double bond in the isobutenyl side chain occurs. Thus, provided R does not contain a group degradable under ozonolysis conditions, the required carbonyl compound XI for this alternative method can be obtained directly by ozonolysis of the chrysanthemate and the ozonolysed chrysanthemate XI used in the Wittig reaction to give the insecticidal ester. Some furan containing compounds are degraded under ozonolysis conditions so the 5-benzyl-3-furylmethyl ester of caronaldehyde cannot be obtained by direct ozonolysis of the corresponding chrysanthemate (it must be obtained in two stages *via* an alkyl ester of caronaldehyde) but a 3-phenoxybenzyl ester can be so treated.

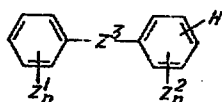
Acids of the general formula IX ($COQ^1=COOH$) where $R^1=R^3=H$ and R^2 =an alkyl group containing at least two carbon atoms can be prepared by reaction between 2-ethynyl-3,3-dimethyl cyclopropane carboxylic acid and an appropriate alkyl halide in the presence of an alkali metal followed by catalytic semi-hydrogenation.

Alcohols and halides of formula VIII are described in British Patent Specification No. 1,305,025.

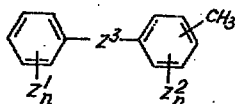
Alcohols of formula VII or VIIIA where D represents CN or $C\equiv CH$ can be prepared by conventional methods from the corresponding aldehydes. Thus, a fur-aldehyde or benzaldehyde can be reacted with (a) HCN, conveniently generated

in situ from KCN and acid, when addition of HCN occurs forming the cyanhydrin or (b) an alkali metal acetylide in liquid ammonia.

Alcohols of formula ROH where R is a group of formula VI where D represents hydrogen may be prepared by reduction of the corresponding acids or esters e.g. with a hydride, or by conversion of the corresponding halide to an ester e.g. by reaction with sodium acetate, followed by hydrolysis of the ester, or by reaction of formaldehyde with a Grignard reagent derived from the corresponding halide. The halides of formula R-halogen where R is a group of formula VI where D represents hydrogen can be prepared by halomethylation of the compound:



or side chain halogenation of:



One or more of the insecticidal esters of the invention may be formulated with an inert carrier or diluent to give insecticidal compositions and these may be prepared, for example, in the form of dusts and granular solids, wettable powders, mosquito coils and other solid preparations or as emulsions, emulsifiable concentrate, sprays and aerosols and other liquid preparations after the addition of the appropriate solvents, diluents and surface active agents.

Pyrethrum synergists such as piperonyl butoxide or tropital, may be added to these compositions. Certain insecticidal esters of the invention show significant superiority over structurally similar esters e.g. chrysanthemates or pyrethrates, in the ability to respond to synergists and many esters of the invention have a synergistic factor several times greater than those exhibited by other synthetic esters. Many of the esters derived from acids of the present invention are much more stable to light than those of previously known acids, and dihalovinyl esters are especially favoured in this connection.

The insecticidal compositions may also include known synthetic pyrethrins to improve kill and/or knock down or to synergise the activity of the known pyrethrin and/or that of the synthetic pyrethrins of the invention.

The new esters of the invention or insecticidal compositions containing them may be used for killing insects or controlling the level of insects on a domestic or agricultural scale by treating the insects themselves or an environment susceptible to insect attack with the compounds or compositions.

The following Examples 6—9, 14—22 and 25—28 are given to illustrate the present invention (temperatures are in °C., refractive indices are measured at 20°C. Examples 1—5, 10—13 and 23—24 describe the preparation of new intermediate compounds. Unless otherwise indicated, the hydrogen atoms at C₁ to C₃ of the cyclopropane ring are in the *trans*-relationship to one another).

EXAMPLE 1.

n-Pentyl triphenylphosphonium iodide (9.5 g., 0.02M), prepared by reaction of *n*-pentyl iodide with triphenylphosphine, was added slowly, under nitrogen, to sodium amide [0.7 g. sodium (0.03M) in liquid ammonia (130 ml.)]. The mixture was stirred for 0.5 hours and the ammonia allowed to evaporate (2 hours). Benzene (130 ml.) was added and the mixture refluxed, under nitrogen, for 0.5 hours, allowed to cool and the supernatant liquid containing the phosphorane decanted off under nitrogen.

The phosphorane solution was added dropwise, under nitrogen, to a stirred solution of methyl *trans*-carboxaldehyde (1.0 g., 0.0064M) (from ozonolysis of methyl ester of (+)-*trans*-chrysanthemic acid) in dry benzene (15 ml.). The addition was completed in 10 minutes and the solution was stirred for a further 0.5 hours. The solution was evaporated, the residue dissolved in diethyl ether, the organic solution washed with water and dried. Evaporation yielded a colourless mixture which was further extracted with petroleum ether (60—80°), evaporation of which yielded a colourless liquid b.p. 107—109°/5 mm., yield (1.07 g., (80%), *n*_D 1.4622) which

was identified by NMR spectroscopy as 2,2-dimethyl-3-(hex-1-enyl)-cyclopropane carboxylic acid methyl ester. (Compound C').

EXAMPLE 2.

The procedure described in Example 1 was repeated replacing the *n*-pentyl iodide with equivalent amounts of *n*-propyl iodide or *n*-butyl bromide, to give alkyl esters of the invention of formula II and of refractive index as indicated below:

Compound	R ²	R ³	R ⁴	R	n _D
A'	C ₂ H ₅	H	H	CH ₃	1.4581
B'	<i>n</i> -C ₃ H ₇	H	H	CH ₃	1.4572

In Compound A', the 3-but-1-enyl substituent is in the *trans* relationship to the cyclopropane ring. Its (+)-*cis*-[1R,3S]-isomer (in free acid form) was made by the following procedure. (In both Compound A' and its *cis* isomer, the configuration around the ethylenic double bond in the 3-substituent is *cis*.)

n-Propylidene phosphorane [prepared by reacting the corresponding phosphonium iodide (7 g.) with sodamide, (sodium (0.7 g.)/liquid ammonia (150 ml.))] in dry benzene (100 ml.) was added dropwise, with stirring, to a solution of the internal hemi-acylal of *cis*-3-formyl-2,2-dimethyl-cyclopropane carboxylic acid (0.7 g.) (French Patent Specification No. 1,580,475) in benzene (10 ml.), under nitrogen. The benzene was evaporated off and the residue dissolved in methylene chloride (75 ml.) and washed with water and sodium carbonate solution. Acidification of the carbonate extract yielded an acid which was extracted with methylene chloride, dried (Na₂SO₄), and evaporated to give (+)-*cis*-[1R,3S]-3-but-1-ene-2,2-dimethyl-cyclopropane carboxylic acid (0.7 g.). (Compound A' *cis*).

EXAMPLE 3.

The procedure described in Example 1 was repeated replacing the methyl trans-coronaldehyde by an equivalent weight of ethyl (±)-*cis-trans*-3-acetyl-2,2-dimethyl-cyclopropane carboxylate and replacing the *n*-pentyl iodide by methyl iodide, ethyl iodide, *n*-propyl iodide, or *n*-butyl bromide to give the alkyl esters of formula II as indicated below having the following refractive index:

Compound	R ²	R ³	R ⁴	R	n _D
F'	H	H	CH ₃	C ₂ H ₅	1.4469
G'	(1) CH ₃	H	CH ₃	C ₂ H ₅	1.4570
H'	(2) C ₂ H ₅	H	CH ₃	C ₂ H ₅	1.4570
I'	<i>n</i> -C ₃ H ₇	H	CH ₃	C ₂ H ₅	1.4573

(1) (2) the stereochemistry of these esters about the double bond αβ to the cyclopropane ring is (1) 40:60 and (2) 80:20 Z:E.

EXAMPLE 4.

A suspension of sodium hydride in oil (0.50 g., approx. 0.0095M NaH) was washed with dry diethyl ether (20 ml.) under nitrogen. Dry dimethylsulphoxide (DMSO) (3.5 ml.) was added and the mixture heated at 80° for 0.5 hours. After cooling, a slurry of *n*-butyl triphenylphosphonium bromide (3.80 g., 0.0104M) (prepared by reaction of *n*-butyl bromide with triphenylphosphine) in DMSO (9 ml.) was added with stirring, the remainder of the slurry being washed in with diethyl ether (10 ml.). The mixture was stirred for 0.5 hours and ethyl 3-acetyl-2,2-dimethyl cyclopropane carboxylate (1.0 g., 0.0054M) was added. The mixture was thoroughly shaken and stirred for 24 hours under nitrogen. Ice was added and the mixture acidified with aqueous potassium hydrogen sulphate. After diethyl ether extraction, the organic solution was washed with water, saturated sodium chloride solution, and evaporation of the dried solution (Na₂SO₄) yielded a solid which on extraction with

petroleum spirit (60—80°) and evaporation yielded a colourless liquid b.p. 112—188°/20 mm., 0.52 g., (43%) n_D 1.4573. This liquid was identified by NMR spectroscopy as the compound of formula II where $R^2=n-C_3H_7$, $R^3=H$, $R^1=CH_3$, and $R=C_2H_5$. (Compound I').

EXAMPLE 5.

Chloromethylenetriphenylphosphonium chloride (2.1 g., 0.006M) and dry piperidine (0.51 g., 0.006M), in dry diethyl ether (15 ml.) was treated, under nitrogen, with 8% *n*-butyl lithium in hexane (4.8 ml., [0.388 g., 0.006M]). The mixture was stirred at room temperature for 1.5 hours and *t*-butyl *trans*-cinnamaldehyde (1.27 g., 0.0064M) in dry benzene (5 ml.) was added. The mixture was left to stir for 3 days and the solution filtered and the residue washed with dry diethyl ether. The filtrate was washed with 10% H_2SO_4 , water and evaporation of the dried (Na_2SO_4) solvent followed by distillation yielded a colourless liquid b.p. 100°/20 mm. (70%). This was identified by NMR spectroscopy as the ester of formula II where $R^3=Cl$, $R^2=H$, $R^1=H$ and $R=t-C_4H_9$ and was found to have n_D 1.4670. The stereochemistry about the double bond $\alpha\beta$ to the ring was 20:80 Z:E.

The alkyl esters whose preparation is described above in Examples 1 to 6 were then converted into the corresponding 5-benzyl-3-furylmethyl ester by the procedures described below in Examples 6—9.

EXAMPLES 6—7.

0.2 mols of sodium were slowly added to a solution of 2 mols of 5-benzyl-3-furylmethyl alcohol in toluene. When the reaction between the sodium and the alcohol to give the sodium alcoholate was complete, a solution containing about 1 molar proportion of the alkyl ester of formula II in toluene was added and the mixture heated under reflux with separation of the methanol or ethanol evolved in the *trans*-esterification reaction. After the solution had cooled, the desired 5-benzyl-3-furylmethyl ester was recovered in yields of 50—70%, based on the weight of alkyl ester, by chromatography on alumina. The structure of the esters as being in accordance with formula II was confirmed by NMR spectroscopy and gas/liquid chromatography.

The following insecticidal esters were prepared:

Compound	R^2	R^3	R^1	n_D
A	C_2H_5	H	H	1.5174 (<i>trans</i> isomer)
A <i>cis</i>	C_2H_5	H	H	1.5347 ((+)- <i>cis</i> -[1R,3S] isomer)
B	<i>n</i> - C_3H_7	H	H	1.5177
C	<i>n</i> - C_4H_9	H	H	1.5128
F	H	H	CH_3^*	1.5157
G	CH_3	H	CH_3^*	1.5206
H	C_2H_5	H	CH_3^*	1.5180
I	<i>n</i> - C_3H_7	H	CH_3^*	1.5118

Compounds A—I are all compounds of formula II where $R=5$ -benzyl-3-furylmethyl. * These compounds are a mixture of ($\pm$)-*cis-trans*-isomers.

Compound A *cis* was prepared from A' *cis* by treating with thionyl chloride in benzene to convert A' *cis* to the acid chloride and then reacting the acid chloride with 5-benzyl-3-furylmethyl alcohol in benzene in the presence of pyridine.

EXAMPLE 8.

Methyl 2,2-dimethyl-3-(but-1-enyl)-cyclopropane carboxylate, (prepared as described in Example 2), (2.8 g.) was refluxed for 1 hour with 1.8 g. NaOH in 70 mls. methanol. The reaction mixture was then diluted with water, acidified and extracted with diethyl ether to give 2.01 g. 2,2-dimethyl-3-(but-1-enyl)-cyclopropane carboxylic acid, n_D 1.4719. The acid was then converted into its acid chloride by reaction with

thionyl chloride and the acid chloride then esterified by reaction in benzene with an equimolar amount of ($\pm$)-allethrolone, (+)-pyrethrolone, 3-benzylbenzyl alcohol or 3-phenoxybenzyl alcohol in the presence of an equimolar amount of pyridine. The reaction mixture was then chromatographed on neutral alumina and the solvent evaporated to give the desired ester. The following insecticidal esters were prepared:

Compound	R ²	R ³	R ¹	R	n _D
Q	C ₂ H ₅	H	H	($\pm$)-allethronyl	1.5009
R	C ₂ H ₅	H	H	(+)-pyrethronyl	1.5159
S	C ₂ H ₅	H	H	3-benzylbenzyl	1.5488
T	C ₂ H ₅	H	H	3-phenoxybenzyl	1.5439

EXAMPLE 9.

A mixture of the *tertiary* butyl ester described in Example 5 (410 mg.) toluene-4-sulphonic acid (47.5 mg.) and dry benzene (15 ml.) were refluxed 2 hours and cooled to give a solution of the corresponding carboxylic acid. Pyridine (163 mg.) and thionyl chloride (213 mg.) were then added, and the mixture allowed to stand for 2 hours to give the acid chloride. A mixture of substantially equimolar proportions of the acid chloride, 5-benzyl-3-furylmethyl alcohol and pyridine was prepared in dry benzene and the mixture cooled and allowed to stand at room temperature overnight. The mixture was then poured through a column of neutral alumina and eluted with benzene to give a compound of formula II where R²=Cl, R³=H, R¹=H and R=5-benzyl-3-furylmethyl. This ester, designated ester K, has n_D 1.5418.

EXAMPLE 10.

Triphenyl phosphine (13 g.) was dissolved in dry benzene (60 ml.) and ethyl bromoacetate (8.3 g.) was added dropwise. The solution was heated at 70° for 2 days, and then cooled and filtered. The residue was washed with benzene and dried to give about 16 g. of (ethoxycarbonylmethyl) triphenylphosphonium bromide. The phosphonium salt (10 g.) was dissolved in water (250 ml.) and 5% aqueous sodium hydroxide was added dropwise with stirring until the solution became alkaline to litmus. The resulting precipitate was filtered off, washed with water and dried. Crystallisation from ethyl acetate/petroleum spirit gave (ethoxycarbonyl methylene) triphenyl phosphorane as a colourless solid in about 80% yield.

The phosphorane (3.2 g., 0.0092M) in dry dichloromethane (30 ml.) was added to *t*-butyl *trans*-cinnamaldehyde (1.5 g., 0.0076M) (from ozonolysis of *t*-butyl (+)-*trans*-chrysanthemic acid) in dichloromethane (30 ml.) with stirring under nitrogen; stirring was continued at room temperature for 2.5 days. The solution was evaporated, and the residue extracted with petroleum spirit (60–80°) which on evaporation and distillation yielded a colourless liquid b.p. 112°/0.7 mm., 1.60 g. (79%) n_D 1.4666 which was identified by NMR spectroscopy and gas/liquid chromatography as a compound of formula II where R²=carboethoxy, R³=H and R=*t*-butyl. (Compound P19/B').

EXAMPLE 11.

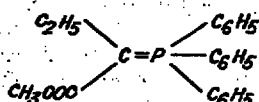
The procedure described in Example 10 was repeated but replacing the bromoacetic acid ethyl ester by an equivalent weight of bromoacetic acid methyl ester and by bromoacetic acid propyl ester and making any necessary variations in reaction time or temperature during phosphorane formation, to give compounds of formula II where R²=H, R=*t*-butyl and R³=carbo-methoxy or carbon-*n*-propoxy, n_D 1.4677 and 1.4723, (compounds P19/A' and P19/C') respectively.

EXAMPLE 12.

The procedure described in Example 10 was repeated replacing the bromoacetic acid ethyl ester by an equivalent weight of α -bromopropionic acid ethyl ester and propyl ester. Esters of formula II were obtained where R²=methyl, R=*t*-butyl and R³=carboethoxy and carbo-*n*-propoxy, n_D 1.4653 and 1.4712 (Compounds P19/D' and P19/E') respectively.

EXAMPLE 13.

n-Propyl triphenyl phosphonium iodide was prepared by the procedure described in Example 10 replacing the ethyl bromoacetate by *n*-propyl iodide. The phosphonium iodide (9.5 g.) was then treated under nitrogen with the NaNH₂, obtained from 0.5 g. Na in 100 mls. liquid NH₃, and the NH₃ allowed to evaporate over 2 hours. Benzene (120 mls.) was then added, the mixture refluxed for 15 minutes and 1.08 g. methyl chloroformate in 50 mls dry benzene then added dropwise. The mixture was refluxed a further 10 minutes and then cooled, filtered and the benzene removed to leave a phosphorane of formula:



as residue.

The phosphorane was then reacted with *t*-butyl caronaldehyde in dichloromethane as described in Example 10 to give a compound b.p. 130°/3 mm., *n*_D 1.4714 identified as in Example 10 as being of formula II where R³=COOCH₃, R²=C₆H₅, R¹=H and R=*t*-butyl. (Compound P19/F¹).

The above procedure was also repeated replacing the methyl chloroformate by ethyl and *n*-propyl chloroformate respectively when the following compounds of formula II were obtained.

	R ³	R ²	R ¹	R	b.p.	<i>n</i> _D
P19/G ¹	COOC ₂ H ₅	C ₆ H ₅	H	<i>t</i> -butyl	114–116°/1 mm.	1.4682
P19/H ¹	COO <i>n</i> -C ₃ H ₇	C ₆ H ₅	H	<i>t</i> -butyl	120°/1 mm.	1.4683.

EXAMPLE 14.

The compound of formula II where R³=*n*-propoxy carbonyl, R²=CH₃ and R¹=*t*-butyl (0.393 g.) described in Example 12 was refluxed 2 hours with toluene 4-sulphonic acid (47.2 mg.) in benzene (11.5 ml.). The solution was cooled and the resulting acid (R³=*n*-propoxycarbonyl, R²=CH₃, R=H) crystallised out. Dry pyridine (0.127 g., 131 μl.) and thionyl chloride (0.158 g. 96 μl) were added and the mixture left to stand for 2 hours at about 20° when the corresponding acid chloride formed.

A solution of 5-benzyl-3-furylmethyl alcohol (275 mg.) and pyridine (0.105 g., 108 μl.) in benzene (8 ml.) was added and the solution left to stand overnight. The resulting solution was passed through a column of neutral alumina and then evaporated to give 550 mg. of a compound of formula II where R³=*n*-propoxycarbonyl, R²=CH₃ and R=5-benzyl-3-furylmethyl, *n*_D 1.5125. (Compound P19/E). The structure of the ester as being in accordance with formula II was confirmed by NMR spectroscopy and gas/liquid chromatography.

The following esters were prepared by similar methods.

Compound	R ²	R ³	<i>n</i> _D
P19/A	H	COOCH ₃	1.5262
P19/B	H	COOC ₂ H ₅	1.5298
P19/C	H	COO <i>n</i> -C ₃ H ₇	1.5278
P19/D	CH ₃	COOC ₂ H ₅	1.5235
P19/E	CH ₃	COO <i>n</i> -C ₃ H ₇	1.5125
P19/F	C ₆ H ₅	COOCH ₃	1.5228
P19/G	C ₆ H ₅	COOC ₂ H ₅	1.5193
P19/H	C ₆ H ₅	COO <i>n</i> -C ₃ H ₇	1.5190

Compounds P19A to P19/H are all compounds of formula II where R=5-benzyl-3-furylmethyl.

EXAMPLE 15.

t-Butyl-*trans*-cinnamaldehyde (1.0 g.) (obtained by ozonolysis of the *t*-butyl ester of (+)-*trans*-chrysanthemic acid) and triphenyl phosphine (2.65 g.) dissolved in dry carbon tetrachloride (10 ml.) were heated, under nitrogen with stirring, at 60° for 7 hours. The reaction mixture was evaporated under reduced pressure and the residue extracted with diethyl ether (≈30 ml.). The organic extract was washed with water, dried (over Na₂SO₄) and evaporated. The residue was extracted with petroleum ether (40–60°) and the solution evaporated and distilled yielding crude product (0.77 g.) (b.p. 100°/1 mm.), which was purified by crystallisation to give *t*-butyl-(+)-*trans*-[1R,3R]-2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylate m.p. 52–3° (Compound P21/A').

EXAMPLE 16.

Triphenyl phosphine (1.32 g.) was added to a well stirred solution of carbon tetrabromide (0.84 g.) in dry dichloromethane (15 ml.). *t*-Butyl-(+)-*trans*-cinnamaldehyde (0.5 g.) was added and the solution was stirred overnight at room temperature. After working up as described in Example 15, the crude product was distilled yielding two fractions (1) b.p. 83–90°/0.7 mm, (0.15 g.), *n*_D 1.4749 (2) b.p. 90–107°/0.7 mm, (0.24 g.), *n*_D 1.4910. The second fraction was shown (glc) to contain ≈95% of the desired *t*-butyl-(+)-*trans*-[1R,3R]-2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylate. (Compound P21/B').

EXAMPLE 17.

The *t*-butyl ester described in Example 15 (280 mg.), was heated at reflux with toluene-4-sulphonic acid (55 mg.) in dry benzene (10 ml.) for 1.5 hour and cooled to give a solution of the corresponding acid. Pyridine (108.5 mg.) and thionyl chloride (126 mg.) were added and the mixture left to stand at room temperature for 2 hours. A solution of pyridine (83.5 mg.) and 5-benzyl-3-furylmethyl alcohol (219 mg.) in dry benzene (5 ml.) was added and the mixture left to stand overnight. After chromatography on neutral alumina, the solution was evaporated to yield 296 mg. of a (+)-*trans*-[1R,3R] compound of formula II where R²=Cl, R³=Cl, R¹=H and R=5-benzyl-3-furylmethyl. This ester, designated ester P21A, has *n*_D 1.5403.

The above procedure was repeated with ester P21/B' described in Example 16 to give (+)-*trans*-[1R,3R] ester P21/B where R²=R³=Br, R¹=H, R=5-benzyl-3-furylmethyl, *n*_D 1.5462.

EXAMPLE 18.

The conversion of the acid to the acid chloride and subsequent esterification using 5-benzyl-3-furylmethyl alcohol as described in Example 17 was repeated replacing the (+)-*trans* acid by other isomers of the acid and, in certain experiments, using 3-phenoxybenzyl or 3-benzylbenzyl alcohol or (±)-allethrolone or (+)-pyrethrolone or 5-propargyl-2-furylmethyl alcohol or 2,3,4,5-tetrahydrophthalimidomethyl alcohol as the alcohol to give the following esters of formula II.

C

P

P

P

P

P

P2

P2

P2

P2

P2

P21

P21

P21

P2

R

py

hy

aci

1,3

cat

pro

sepi

cis

tem

prec

and

isom

a)

in d

Benz

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The

soluti

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Yield

b)

(

0.3 g

was s

dropw

Compound	R ³	R ²	R ¹	Configuration	m.p. °	n _D
P21C	Cl	Cl	H	(±)- <i>trans</i>	61	1.5518
P21D	Cl	Cl	H	(±)- <i>cis</i>	43	1.5485
P21E	Cl	Cl	H	(±)- <i>cis-trans</i>	48.58	1.5445
P21F	Cl	Cl	H	(±)- <i>trans</i>		1.5607
P21G	Cl	Cl	H	(±)- <i>cis</i>		1.5654
P21H	Cl	Cl	H	(±)- <i>cis-trans</i>		1.5694
P21I	Cl	Cl	H	(±)- <i>trans</i>		1.5633
P21J	Cl	Cl	H	(±)- <i>cis</i>		1.5654
P21K	Cl	Cl	H	(±)- <i>cis-trans</i>		1.5701
P21L	Cl	Cl	H	(±)- <i>trans</i>		1.5136
P21M	Cl	Cl	H	(±)- <i>trans</i>		1.5324
P21Q	Cl	Cl	H	(±)- <i>trans</i>		1.5237(n _D ²³)
P21S	Cl	Cl	H	(±)- <i>trans</i>		1.5333(n _D ²³)

In compounds P21C, P21D and P21E, R=5-benzyl-3-furylmethyl, in compounds P21F, P21G and P21H, R is 3-phenoxybenzyl, in compounds P21I, P21J, and P21K, R is 3-benzylbenzyl, in compound P21L, R is (±)-allethronyl, in P21M, R is (+)-pyrethronyl in P21Q, R is 5-propargyl-2-furylmethyl and P21S, R is 2,3,4,5-tetrahydrophthalimidomethyl."

The starting acid was prepared by a variant on the conventional chrysanthemic acid synthesis using ethyldiazoacetate in which, in this case, 1,1-dichloro-4-methyl-1,3-pentadiene was reacted with ethyldiazoacetate in the presence of the copper catalyst and the resulting ethyl (±)-*cis-trans*-2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylate hydrolysed to the free acid. The *cis*- and *trans*-isomers can be separated from one another by selective crystallisation from *n*-hexane in which the *cis* isomer is more soluble. The isomeric mixture was dissolved in hexane at room temperature and cooled to 0° or -20°C., when the *trans*-isomer precipitates. This precipitate was ground up, washed with a small volume of hexane at room temperature and the residue recrystallised again from hexane at 0° or -20°C., to give the *trans*-isomer as a residue. The *cis*-isomer is recovered from the hexane solution.

EXAMPLE 19.

a) 5-Benzyl-3-furylaldehyde

Chromium trioxide (3.00 g.) was added to a stirred solution of pyridine (4.75 g.) in dry methylene chloride (75 ml.), and stirring was continued for 15 minutes. 5-Benzyl-3-furylmethyl alcohol (0.94 g.) was added and the mixture stirred for 15 minutes. The mixture was filtered and the residue washed with ether (100 ml). The filtrate and washings were combined and washed with 5% sodium hydroxide solution (3×50 ml.), 2.5N hydrochloric acid (50 ml.) and 5% sodium carbonate solution (50 ml.) and dried (Na₂SO₄). Yield=(0.53 g.), b.p. 116°/0.8 mm.Hg, n_D=1.5652.

b) (±)-α-Cyano-5-benzyl-3-furylmethyl alcohol

The aldehyde (1) (0.53 g.) was added to a solution of potassium carbonate (0.3 g.) in water (3 ml.) and dioxan (5 ml.) was added to effect solution. The solution was stirred for 10 minutes at 15°C., when 40% sulphuric acid (1 ml.) was added dropwise, stirring being continued for a further 10 minutes. The mixture was extracted

with carbontetrachloride (50 ml.) and dried (Na_2SO_4). Evaporation yielded the product (0.53 g.) n_D 1.5377. (The structure was confirmed by NMR).

c) $(\pm)$ - α - Cyano - 5 - benzyl - 3 - furylmethyl - $(\pm)$ - *cis* - *trans* - 3 - (2,2'-dichlorovinyl) - 2,2 - dimethyl cyclopropane carboxylate (Compound P21/N).

A mixture of the alcohol (265 mg.) prepared as described above, and 80 mg. pyridine in 10 ml. dry benzene was added to 277 mg. of $(\pm)$ -*cis-trans*-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxylic acid chloride in 10 ml. dry benzene. The resulting mixture was left overnight and then column chromatographed on neutral alumina. Evaporation of solvent gave 0.31 g. of Compound P21/N, n_D 1.5428 (Structure confirmed by NMR).

EXAMPLE 20.

a) 3-Phenoxybenzaldehyde

Chromium trioxide (3.00 g.) was added to a stirred solution of pyridine (4.75 g.) in dry methylene chloride (75 ml.), and stirring was continued for a further 15 minutes. 3-Phenoxybenzyl alcohol (1 g.) in methylene chloride (5 ml.) was added, the mixture stirred for a further 15 minutes, decanted and the residue washed with diethyl ether (100 ml.). The filtrate was washed with 5% sodium hydroxide solution (3×50 ml.), 2.5 N HCl (50 ml.) and 5% sodium carbonate solution (50 ml.) and dried over Na_2SO_4 to give 3-phenoxy-benzaldehyde. Yield (0.80 g.), b.p. $126^\circ/0.8$ mm.Hg, n_D = 1.5984.

b) $(\pm)$ -(α -Cyano)-3-phenoxybenzyl alcohol

3-Phenoxybenzaldehyde (0.8 g.) was added to a solution of potassium cyanide (0.3 g.) in water (1 ml.) at 15° . Slowly during 10 minutes 40% sulphuric acid (1 ml.) was added dropwise, stirring being continued for a further 15 minutes. The mixture was extracted with carbontetrachloride (40 ml.), dried (Na_2SO_4) and evaporated to yield 0.64 g. of $(\pm)$ - α -cyano-(3-phenoxy)-benzylalcohol. n_D = 1.5832 (Structure confirmed by NMR).

c) This α -cyano alcohol described above (247 mg.), pyridine (79 mg.) and $(\pm)$ -*cis/trans*-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropane carboxylic acid chloride (227 mg.) were reacted at 20°C ., in benzene (20 ml.) solution for 18 hours, which after chromatography on neutral alumina and evaporation of the solvent yielded $(\pm)$ - α - cyano - 3 - phenoxybenzyl - $(\pm)$ - *cis* - *trans* - 3 - (2,2 - dichlorovinyl) - 2,2-dimethyl cyclopropane carboxylate (Compound P21/P) (260 mg.), n_D 1.5561. (Structure confirmed by NMR).

EXAMPLE 21.

a) 3-Benzylbenzaldehyde

Benzylbenzyl alcohol (1 g.) was oxidised using the chromium trioxide/pyridine complex as described in Example 20 a) yielding the aldehyde (0.67 g.), b.p. $124^\circ\text{C}/0.2$ mm, n_D^{20} = 1.6010.

b) $(\pm)$ -(α -Cyano)-3-benzylbenzyl alcohol

The prepared aldehyde (0.67 g.) underwent the reactions described in Example 20 b) to form the required cyanohydrin (0.41 g.), n_D^{20} = 1.5703.

$(\pm)$ - (α - Cyano) - 3 - benzylbenzyl - $(\pm)$ - *cis/trans* - (2,2 - dichlorovinyl) - 2,2 - dimethylcyclopropane carboxylate (Compound P21/Q) of n_D 1.5462 was prepared from the alcohol of b) above and the acid chloride following the procedure of Example 20 c).

EXAMPLE 22.

a) 3'-Phenoxybenzyl-3-formyl-2,2-dimethylcyclopropane carboxylate.

3-Phenoxybenzyl-(+)-*trans*-chrysanthemate (2.0 g.) in methanol (500 g.) at -70°C ., was subjected to a stream of ozone for 30 minutes. Nitrogen was passed through the solution and dimethyl sulphide (1.5 g.) added. It was allowed to warm to room temperature and stirred overnight. The solvent was evaporated and acetone (30 ml.) and 30% acetic acid (20 ml.) was added, the solution being allowed to stand for 30 minutes at 80°C . It was poured onto water (200 ml.) and extracted with ether (200 ml.). After washing with sodium carbonate solution the organic solution was dried (Na_2SO_4) and evaporated to give the title aldehyde. Yield (1.69 g.) n_D^{20} = 1.5558.

b) The procedure described in Example 15 was repeated using 3'-phenoxybenzyl-3-formyl-2,2-dimethyl cyclopropane carboxylate in place of *t*-butylcaronaldehyde to give compound P21F (see Example 18) directly.

EXAMPLE 23.

Triphenyl phosphine (13 g.) was dissolved in dry benzene (60 ml.) and methyl bromoacetate (8.3 g.) was added dropwise. The solution was heated at 70°C., for 2 days, and then cooled and filtered. The residue was washed with benzene and dried to give about 16 g. of (methoxycarbonyl methyl)triphenylphosphonium bromide. The phosphonium salt (10 g.) was dissolved in water (250 ml.) and 5% aqueous sodium hydroxide was added dropwise with stirring until the solution became alkaline to litmus. The resulting precipitate was filtered off, washed with water and dried. Crystallisation from ethyl acetate/petroleum spirit gave (methoxycarbonyl methylene)triphenyl phosphorane as a colourless solid in about 80% yield.

(Methoxycarbonylmethyl)triphenylphosphorane (3.34 g.) in methylene chloride (70 ml.) was cooled to -70°C., triethylamine (1.01 g.) was added with stirring followed by chlorine (0.77 g.) in CCl₄ (11 mls). Stirring was continued for 30 minutes at this temperature and for 1 hour while the reaction mixture warmed to room temperature. The reaction mixture was washed with water (3 × 50 ml.), dried over Na₂SO₄ and evaporated to yield 2.9 g of chlorinated phosphorane / Ph₃P = C(Cl)COOMe.

A mixture of *t*-butyl-trans-caronaldehyde (from ozonolysis of *t*-butyl ester of (+)-trans-chrysanthemic acid) (0.7 g.) and the chlorinated phosphorane (1.3 g.) in 10 ml. dry benzene was refluxed for one hour. After distillation of the benzene, the resulting product was distilled under reduced pressure to give *t*-butyl-2,2-dimethyl-3-(2-chloro-2-carbomethoxyvinyl)-cyclopropyl carboxylate, b.p. 110°C./0.4 mm, n_D^{20} 1.4749 (Yield, 0.65 g.).

This compound was designated Compound P24A'.

EXAMPLE 24.

The procedure described in Example 23 was repeated replacing the methyl bromoacetate by ethylbromoacetate or propylbromoacetate and by replacing the methylbromoacetate by ethylbromoacetate and replacing chlorine by bromine in the halogenation of the phosphorane step. The following compounds of formula II were obtained.

Compound	R	R ¹	R ²	b.p.	n_D^{20}
P24B'	<i>t</i> -butyl	COOC ₂ H ₅	Cl	110-112°C/0.4mm	1.4883
P24C'	<i>t</i> -butyl	COO <i>n</i> -C ₃ H ₇	Cl	160-180°C/0.8mm	1.4688
P24D'	<i>t</i> -butyl	COOC ₂ H ₅	Br	120-124°C/0.04mm	1.4830

EXAMPLE 25.

A mixture of compound P24A' of Example 23 (320 mg.) and toluene-4-sulphonic acid (50 mg.) in dry benzene (10 ml.) were refluxed for approximately 2 hours and then cooled. 2,2-Dimethyl-3-(2-chloro-2-carbomethoxyvinyl)-cyclopropane carboxylic acid was identified in the solution by NMR. Pyridine (111 mg., 114 microlitres) and thionyl chloride (132 mg., 80 microlitres) were added to the solution of the carboxylic acid and the mixture was left for 3 hours at room temperatures. 2,2-Dimethyl-3-(2-chloro-2-carbomethoxyvinyl)-cyclopropane carboxylic acid chloride was identified in the solution by NMR. A solution of 5-benzyl-3-furylmethyl alcohol (210 mg.) and pyridine (88 mg., 90 microlitres) in dry benzene (5 ml.) was added and the mixture left overnight at room temperature. The solution was then run through a column of neutral alumina and eluted with benzene to give 200 mg. of the 5-benzyl-3-furylmethyl ester of 2,2-dimethyl-3-(2-chloro-2-carbomethoxyvinyl)-cyclopropane carboxylic acid, n_D^{20} 1.5398. This compound was designated compound P24A.

EXAMPLE 26.

The procedure described in Example 25 was repeated using compounds P24B', P24C' and P24D' of Example 24 and the following compounds of formula II were obtained.

Compound	R ¹	R ²	n _D ²⁰
P24B	COOC ₂ H ₅	Cl	1.5404
P24C	COO _n -C ₃ H ₇	Cl	1.5332
P24D	COOC ₂ H ₅	Br	1.5366

The above three compounds are compounds of formula II where R represents 5-benzyl-3-furylmethyl.

EXAMPLE 27.

Methyl-(+)-*cis*-caronaldehyde was obtained by ozonolysis of methyl (+)-*cis*-chrysanthemate. The procedure described in Example 16 was then repeated using 5.3 g. triphenylphosphine, 3.36 g. carbon tetrabromide and 60 mls. dry dichloromethane and 1.5 g. methyl-(+)-*cis*-caronaldehyde. The reaction product was then refluxed 3 hours with 9 mls. acetic acid, 6 mls. concentrated HBr and 3 mls. water and then diluted with water and extracted with ether. The organic solution was extracted with dilute sodium hydroxide and this extract acidified and extracted with ether and evaporated to give a residue of (+)-*cis*-[1R,3S]-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropane carboxylic acid.

The carboxylic acid described above was converted to its acid chloride by reaction with thionylchloride in pyridine as described in Example 17 and the resulting acid chloride reacted with 3-phenoxybenzyl alcohol in dry benzene in the presence of pyridine as described in Example 17 to give 3-phenoxy-benzyl (+)-*cis*-[1R,3S]-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropane carboxylate, mp 93°, n_D 1.5848 (Compound P29A).

The esterification described above was repeated replacing 3-phenoxybenzyl alcohol by (±)-α-cyano-3-phenoxybenzyl alcohol to give (±)-α-cyano-3-phenoxybenzyl (+)-*cis*-[1R,3S]-2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylate, n_D 1.5732 (Compound P29B).

EXAMPLE 28.

The esterification procedures described in Example 27 were repeated replacing the (+)-*cis*-dibromovinyl acid by (+)-*trans*-(1R,3R)-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropane carboxylic acid (obtained as described in Example 16 and 17), (+)-*trans*-[1R,3R]-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropane carboxylic acid (prepared as described in Example 15 and 17) and (±)-*cis-trans*-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropane carboxylic acid prepared as described in Example 18. The following esters were prepared:

3 - phenoxybenzyl (+) - *trans* - (1R,3R) - 2,2 - dimethyl - 3 - (2,2 - dibromovinyl) cyclopropane carboxylate, n_D 1.5828 (Compounds P29C).

(±) - α - cyano - 3 - phenoxybenzyl (+) - *trans* - [1R,3R] - 2,2 - dimethyl - 3 - (2,2 - dibromovinyl) cyclopropane carboxylate, n_D 1.5664 (Compound P29D).

(±) - α - cyano - 3 - phenoxybenzyl (+) - *trans* - [1R,3R] - 2,2 - dimethyl - 3 - (2,2 - dichlorovinyl) cyclopropane carboxylate n_D 1.5498 (Compound P29E).

(±) - α - cyano - 3 - phenoxybenzyl (±) - *cis-trans* - 2,2 - dimethyl - 3 - (2,2 - dichlorovinyl) cyclopropane carboxylate, n_D 1.5632 (Compound P29F).

The following formulations are given to illustrate the way in which the insecticidal compounds of the invention can be applied to insects or environments susceptible to insect attack.

Formulation 1.

Oil-based liquid spray for household insects

active compound	0.015% w/v
25% Pyrethrum Extract	0.25%
Piperonyl butoxide	0.5%
Antioxidant	0.1%

Odourless light oil solvent e.g. xylene to make 100 vols.

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Formulation 2.

Water-based liquid spray concentrate for mosquito control

active compound	0.25% w/v
Piperonyl butoxide	1.0%
Non-ionic emulsifier	0.25%
Antioxidant	0.1%
Water to make	100 vols.

This concentrate should be diluted 1:80 v/v with water before spraying.

Formulation 3.

Aerosol

active compound	0.05% w/w
25% Pyrethrum Extract	0.8%
Piperonyl butoxide	1.5%
Odourless petroleum distillate (b.p. 200—265°C)	17.338%
Propellant, e.g. a mixture of equal quantities of trichloromonofluoromethane and dichlorodifluoromethane	80.0%
Perfume	0.2%
Antioxidant	0.1%

Formulation 4.

Mosquito coil

active compound	0.25% w/w
Tabu powder (also known as pyrethrum marc)	30.0%
Filler(s), e.g. wood flour, powdered leaves or nut shells	68.75%
Brilliant Green	0.5%
p-Nitrophenol	0.5%
(Tabu is a Registered Trade Mark)	

Formulation 5.

Emulsifiable concentrate

active compound	1.5% w/w
Non-ionic emulsifier	25.0%
Xylene	73.4%
Antioxidant	0.1%

This concentrate may then be diluted at the rate of 30 mls. to 4 1/2 litres of water prior to use.

Formulation 6.

General purpose powder for household garden, livestock or grain storage use

active compound	0.05% w/w
Tropital (the synergist piperonyl-bis-2-[2'-n-butoxyethoxy]ethyl acetal)	0.25%
Antioxidant, e.g. butyl hydroxy toluene or butyl hydroxy anisole	0.03%
Filler	99.67%

The insecticidal activity of the esters of the invention was assessed against houseflies and mustard beetles using the following techniques:

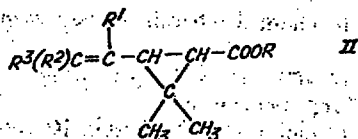
Houseflies (*Musca domestica*)

Female flies were treated on the thorax with a one microlitre drop of insecticide dissolved in acetone. Two replicates of 15 flies were used at each dose rate and 6 dose rates were used per compound under test. After treatment, the flies were maintained at a temperature of 20°C. ± 1° and kill was assessed 24 and 48 hours after treatment. LD₅₀ values were calculated in micrograms of insecticide per fly and relative toxicities were calculated from the inverse ratios of the LD₅₀ values. (See Sawicki *et al*, Bulletin of the World Health Organisation, 35,893, (1966) and Sawicki *et al*, Entomologia and Exp. Appl. 10, 253, (1967)).

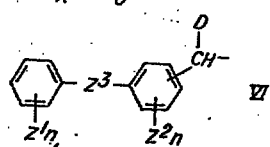
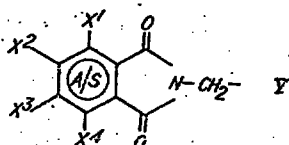
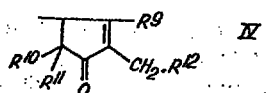
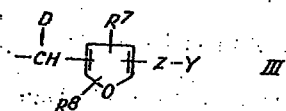
Active compound	LD ₅₀		Approx. Synergistic factor
	active compound only	active compound + synergist	
5-benzyl-3-furyl methyl (+)- <i>trans</i> - chrysanthemate	0.0054	0.00057	9.4
5-benzyl-3-furyl methyl (±)- <i>cis-trans</i> - chrysanthemate	0.010	0.00079	13
P21C	0.0065	0.00033	19
P21D	0.0058	0.00046	12
P21F	0.013	0.00033	39
P21G	0.0083	0.00037	22
A[(+)- <i>trans</i> -(3- <i>cis</i> -but-1-enyl)- isomer]	0.0042	0.00033	13
A[(+)- <i>cis</i> -(3- <i>cis</i> - but-1-enyl)-isomer]	0.0074	0.0012	6

WHAT WE CLAIM IS:—

1. A compound of the general formula:—



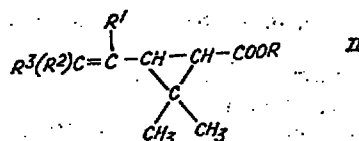
wherein: R¹ represents hydrogen or a methyl group; R² represents hydrogen or a halogeno or alkyl group; R³ represents hydrogen or a halogeno, or carboalkoxy group which contains at least 2 carbon atoms in the alkoxy residue when R² represents methyl; with the proviso that (a) R² and R³ each represent hydrogen only when R¹ represents methyl and (b) when R¹ and R³ represent hydrogen, R² represents alkyl; that alkyl group contains at least 2 carbon atoms, and R represents a group of formula:



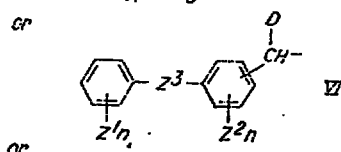
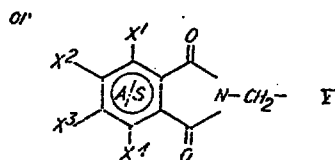
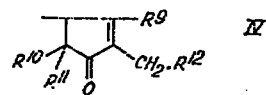
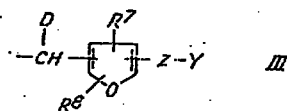
Active compound	LD ₅₀		Approx. Synergistic factor
	active compound only	active compound + synergist	
5-benzyl-3-furyl methyl (+)- <i>trans</i> - chrysanthemate	0.0054	0.00057	9.4
5-benzyl-3-furyl methyl (±)- <i>cis-trans</i> - chrysanthemate	0.010	0.00079	13
P21C	0.0065	0.00033	19
P21D	0.0058	0.00046	12
P21F	0.013	0.00033	39
P21G	0.0083	0.00037	22
A[(+)- <i>trans</i> -(3- <i>cis</i> -but-1-enyl)- isomer]	0.0042	0.00033	13
A[(+)- <i>cis</i> -(3- <i>cis</i> - but-1-enyl)-isomer]	0.0074	0.0012	6

WHAT WE CLAIM IS:—

1. A compound of the general formula:—



5 wherein R¹ represents hydrogen or a methyl group; R² represents hydrogen or a
halogeno or alkyl group; R³ represents hydrogen or a halogeno, or carbo-
10 alkoxy group which contains at least 2 carbon atoms in the alkoxy
residue when R² represents methyl; with the proviso that (a) R² and R³ each represent
hydrogen only when R¹ represents methyl and (b) when R¹ and R³ represent hydrogen,
R² represents alkyl, that alkyl group contains at least 2 carbon atoms, and R represents
a group of formula:



**Mustard Beetles (*Phaedon cochleariae* Fab)**

Acetone solutions of the test compound were applied ventrally to adult mustard beetles using a micro drop applicator. The treated insects were maintained for 48 hours after which time kill is assessed. Two replicates of 40 to 50 mustard beetles were used at each dose level and 3 to 4 dose levels were used for each compound. Again, LD₅₀ values were calculated and relative toxicities were calculated for the inverse ratios of LD₅₀ (see Elliott *et al*, J. Sci. Food Agric. 20, 561, (1969)).

Relative toxicities were calculated by comparison with 5-benzyl-3-furylmethyl (+)-*trans*-chrysanthemate which is one of the most toxic chrysanthemate esters known to houseflies and mustard beetles, its toxicity being about 24 times that of allethrin to houseflies and 65 times that of allethrin to mustard beetles.

The following relative toxicities were obtained.

Compound	Relative Toxicity	
	Houseflies	Mustard Beetles
5-benzyl-3-furylmethyl	1000	1000
(+)- <i>trans</i> -chrysanthemate		
Pyrethrin I	12	1600
Bioallethrin	60	20
A	1700	2000
B	630	890
C	270	420
F	21	—
G	18	—
H	<7	10
I	<7	<10
K	1300	1600
Q	60	69
R	30	300
S	120	170
T	240	300
P19A	91	100
P19B	67	320
P19C	24	40
P19D	290	440
P19E	290	500
P19F	130	360
P19G	300	500
P19H	20	50

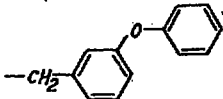
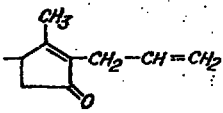
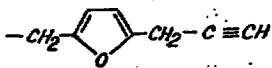
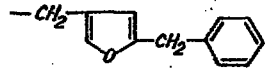


Compound	Houseflies	Mustard Beetles
P21A	2500	2700
P21B	1100	1900
P21C	1000	2200
P21D	1200	1700
P21E	700	1800
P21F	400	790
P21G	680	780
P21H	660	740
P21I	170	420
P21J	360	350
P21K	340	350
P21L	72	73
P21M	19	370
P21N	100	2000
P21P	1300 at least	5000
P24A	82	310
P21B	150	310
P24C	53	120
P24D	450	290
P29A	2200	1600
P29B	10000	11000
P29C	1100	4000
P29D	4100	5200
P29F	1700	

Mammalian toxicity of certain esters of the invention has been determined in rats with the following results:

Compound	LD ₅₀ (mg./kg) to rats.	
	oral	intravenous
pyrethrin I	260-420	2-5
5-benzyl-3-furymethyl		
(+)-trans chrysanthemate	>8000	340
A	800-1000	120
P21E	40	5
P21C	>400	26-33

The insecticidal activity and mammalian toxicity of certain esters of ($\pm$)-*trans*-2,2 - dimethyl - 3 - (2,2 - dichlorovinyl)cyclopropane carboxylic acid has been tested in a further series of experiments with the following results:

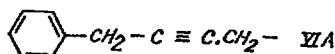
R	Insecticidal activity		Mammalian toxicity	
	Houseflies * ¹	German Cockroaches* ²	oral acute	LD ₅₀ mg/kg
	10.5 mg/100	0.83γ/insect	>300	>300
	55 mg/100 ml.	4.2γ/insect	—	—
	13 mg/100 ml.	6.7γ/insect	300	approximately 300
	4.5 mg/100 ml.	0.54γ/insect	—	100
	Pyrethrin: 200–300 mg/100 ml.	5-benzyl-3-furyl-methyl (+)- <i>cis-trans</i> -chrysanthemate 0.62 γ/insect Pyrethrin: 0.8–1.4γ/insect		Pyrethrin 130

*¹ turn table method

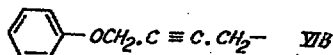
*² topical application method

The synergisability of certain esters of the invention has been determined in tests in which the LD₅₀ of the insecticide in μg. per female fly was determined by the above described methods in untreated flies and in flies pretreated with 2 μg. per fly of the synergist sesamex (2 - (3,4 - methylene dioxyphenoxy) - 3,6,9 - trioxa undecane). The following results were obtained.





or



wherein Z represents O, S, CH₂ or CO, Y represents hydrogen or an alkyl, alkenyl or alkynyl group or an aryl or furyl group which is unsubstituted or substituted in the ring by one or more alkyl, alkenyl, alkoxy or halogeno groups, R¹ and R², which may be the same or different, each represent hydrogen or an alkyl, or alkenyl group,

R³ represents hydrogen or a methyl group,

R¹⁰ and R¹¹, which may be the same or different, each represent hydrogen or an alkyl group,

R¹² represents an organic radical having carbon-carbon unsaturation in a position α to the CH₂ group to which R¹² is attached,

(A/S) indicates an aromatic ring or a dihydro or tetrahydro analogue thereof,

X¹, X², X³ and X⁴, which may be the same or different, each represent hydrogen, chlorine or a methyl group,

Z³ represents —CH₂— or —O— or —CO— or —S—,

D represents H, CN or —C≡CH,

Z¹ and Z², which may be the same or different, each represent chlorine or a methyl group and each n, which may be the same or different is 0, 1 or 2, with the proviso that R does not represent an allethronyl group when R¹ represents hydrogen, R² and R³ each represent chlorine and the compound is racemic.

2. A compound according to claim 1 wherein R² represents hydrogen or a halogeno or alkyl group and R³ represents hydrogen.

3. A compound according to claim 2 wherein R represents hydrogen.

4. A compound according to claim 2 wherein R² represents an alkyl group of 2 to 4 carbon atoms.

5. A compound according to claim 4 wherein R² represents ethyl, *n*-propyl or *n*-butyl.

6. A compound according to any one of the preceding claims wherein R¹ and R³ each represents hydrogen and R² represents ethyl.

7. A compound according to claim 1 or 2 wherein R² represents halogen.

8. A compound according to claim 7 wherein the halogen is chlorine.

9. A compound according to claim 7 or 8 wherein R¹ and R³ each represent hydrogen.

10. A compound according to any one of claims 2—9 wherein D represents hydrogen.

11. A compound according to claim 1 wherein R³ represents a carboalkoxy group (containing at least 2 carbon atoms in the alkoxy residue when R² represents methyl), R² represents hydrogen or an alkyl group and R¹ represents hydrogen.

12. A compound according to claim 11 wherein R² represents hydrogen, methyl or ethyl.

13. A compound according to claim 11 or 12 wherein the alkoxy residue is methoxy, ethoxy or *n*-propoxy.

14. A compound according to any one of claims 11—13 wherein D represents hydrogen.

15. A compound according to claim 1 wherein R² and R³, which may be the same or different, each represent halogen.

16. A compound according to claim 15 wherein the halogen is fluorine or chlorine or bromine.

17. A compound according to claim 15 or 16 wherein R² and R³ each represent chlorine or each represent bromine.

18. A compound according to any one of claims 15—17 wherein D represents hydrogen.

19. A compound according to claim 1 wherein R³ represents a carboalkoxy group, R² represents halogen and R¹ represents hydrogen.

20. A compound according to claim 19 wherein the alkoxy residue is methoxy, ethoxy, or *n*-propoxy.

21. A compound according to claim 19 or 20 wherein the halogen is chlorine or bromine.





22. A compound according to any one of claims 19—21 wherein D represents hydrogen.

23. A compound according to any one of claims 2—9, 11—13, 15—17 or 19—21 wherein D represents CN or $C\equiv CH$.

24. A compound according to claim 1 wherein at least one of R^2 and R^3 is halogen and R^1 is hydrogen.

25. A compound according to any one of the preceding claims wherein R represents a 3-furylmethyl group of formula III wherein R^7 and R^8 each represent hydrogen or a methyl group, Z represents CH_2 , O or CO and Y represents a phenyl group which is unsubstituted or substituted in the ring by a methyl, methoxy, or chlorine group.

26. A compound according to claim 25 wherein R is 5-benzyl-3-furylmethyl.

27. A compound according to any one of claims 1—9, 11—13, 15—17, 19—22 or 24 wherein R represents a cyclopentenonyl group of formula IV or a phthalimidomethyl group of formula V.

28. A compound according to claim 27 wherein R is allethronyl, pyrethronyl or tetrahydro-phthalimidomethyl.

29. A compound according to any one of claims 1 to 24 wherein R is a substituted benzyl group of formula VI wherein each n represents zero and Z^3 represents O or CH_2 .

30. A compound according to claim 29 wherein R represents 3-benzylbenzyl or 3-phenoxybenzyl.

31. A compound according to any one of claims 1—24 wherein R represents α -cyano-3-phenoxy-benzyl, α -cyano-3-benzylbenzyl or α -cyano-5-benzyl-3-furylmethyl.

32. A compound according to claim 10 wherein R is 5-benzyl-3-furylmethyl, 3-phenoxybenzyl or 3-benzylbenzyl.

33. A compound according to claim 14 wherein R is 5-benzyl-3-furylmethyl, 3-phenoxybenzyl or 3-benzylbenzyl.

34. A compound according to claim 18 wherein R is 5-benzyl-3-furylmethyl, 3-phenoxybenzyl or 3-benzylbenzyl.

35. A compound according to claim 22 wherein R is 5-benzyl-3-furylmethyl, 3-phenoxybenzyl or 3-benzylbenzyl.

36. A compound according to claim 23 wherein R is α -cyano-5-benzyl-3-furylmethyl, α -cyano-3-phenoxy-benzyl or α -cyano-3-benzylbenzyl.

37. A compound according to any one of the preceding claims wherein the 3-substituent on the cyclopropane ring is in the *trans* configuration to the cyclopropane ring.

38. Each and every compound according to claim 1 hereinbefore specifically mentioned.

39. 5-Benzyl-3-furylmethyl 2,2-dimethyl-3-(but-1-enyl)-cyclopropane carboxylate.

40. 5-Benzyl-3-furylmethyl 2,2-dimethyl-3-(2-chlorovinyl)-cyclopropane carboxylate.

41. 5-Benzyl-3-furylmethyl 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylate.

42. 5-Benzyl-3-furylmethyl 2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropane carboxylate.

43. 3-Phenoxybenzyl 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylate.

44. α -Cyano-5-benzyl-3-furylmethyl 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylate

45. α -Cyano-3-phenoxybenzyl 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylate.

46. 3-Phenoxy-benzyl 2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropane carboxylate.

47. α -Cyano-3-phenoxybenzyl 2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylate.

48. A compound according to any one of claims 39—47 in the form of a (+)-*cis* isomer, the stereochemistry referring to the cyclopropane ring.

49. A compound according to any one of claims 39—47 in the form of a (+)-*trans*-isomer; the stereochemistry referring to the cyclopropane ring.

50. A compound according to any one of claims 39—47 in the form of a ($\pm$)-*trans* isomer, the stereochemistry referring to the cyclopropane ring.

51. A compound according to any one of claims 39—47 in the form of a ($\pm$)-*cis*-isomer, the stereochemistry referring to the cyclopropane ring.

52. A compound according to any one of claims 39—47 in the form of a ($\pm$)-*cis-trans*-isomer, the stereochemistry referring to the cyclopropane ring.



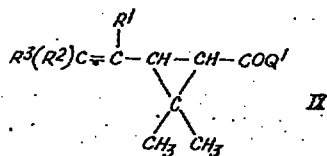
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53. ($\pm$)- α -cyano-3-phenoxybenzyl (+)-*cis*-[1*R*,3*S*]-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropane carboxylate.

54. A process for the preparation of a compound as defined in claim 1 wherein a cyclopropane carboxylic acid or esterifiable derivative thereof of formula:



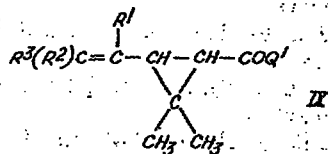
is reacted with an alcohol or esterifiable derivative thereof of formula RQ where R^1 , R^2 , R^3 and R are as defined in claim 1 and Q^1 and Q are functional groups which react together to form an ester linkage.

55. A process according to claim 54 wherein Q^1 represents OH or a halogeno group and Q represents OH.

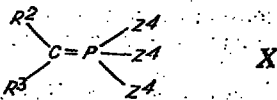
56. A process according to claim 54 wherein Q^1 represents O^-M^+ where M is a silver or triethylammonium cation and Q represents halogen.

57. A process according to claim 54 wherein, except when R or R^3 contain a base sensitive group, Q^1 represents O-alkyl where the alkyl group contains 1 to 6 carbon atoms and Q represents OH, and the *trans*-esterification is carried out in the presence of a base.

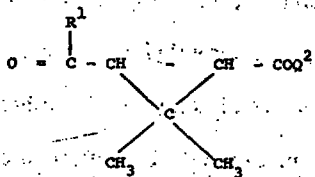
58. A process according to any one of claims 54—57 wherein the esterifiable derivative of formula:



is prepared by reacting a phosphorane of formula

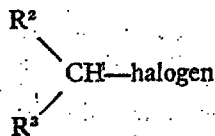


with a carbonyl compound of formula



where R^1 , R^2 and R^3 are as defined in claim 1, Z^4 represents an organic residue which forms a stable triorgano phosphorus oxide and Q^2 represents an alkoxy group and, if desired, converting the resulting alkyl ester into another esterifiable derivative.

59. A process according to claim 58 wherein the phosphorane X is prepared by reacting a substituted methyl halide of formula



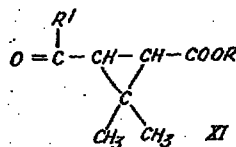
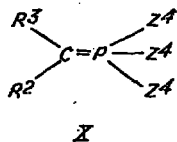
with a triorgano phosphine of formula $P(Z^4)_3$ and, if necessary, treating the resulting quaternary phosphonium halide with a base to bring about dehydrohalogenation.

60. A process according to claim 54 substantially as hereinbefore described.

61. A compound obtained by a process according to any one of claims 54—60.

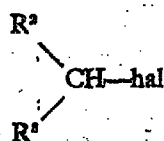


62. A process for preparing a compound as defined in claim 1 which comprises reacting a phosphorane of formula X with a cyclopropane derivative of formula XI:



wherein R, R¹, R² and R³ are as defined in claim 1 and Z⁴ is an organic radical which forms a stable triorganophosphorus oxide.

63. A process according to claim 62 wherein the phosphorane is prepared by reacting a substituted methyl halide of formula:



with a triorgano phosphine of formula P(Z⁴)₃ and if necessary, treating the resulting quaternary phosphonium halide with a base to bring about dehydrohalogenation.

64. A process according to any one of claims 54—59 wherein the compound produced is in accordance with any one of claims 10, 32, 39 or 40.

65. A process according to any one of claims 54—59 wherein the compound produced is in accordance with claim 14 or 33.

66. A process according to any one of claims 54—59 wherein the compound produced is in accordance with any one of claims 18, 34, 41, 42, 43 or 46.

67. A process according to any one of claims 54—59 wherein the compound produced is in accordance with claim 22 or 35.

68. A process according to any one of claims 54—59 wherein the compound produced is in accordance with any one of claims 23, 36, 44, 45 or 47.

69. A process according to any one of claims 54—59 wherein the compound produced is in accordance with claim 53.

70. A process according to claim 62 substantially as hereinbefore described.

71. A compound prepared by a process according to any one of claims 62, 63 or 70.

72. A compound prepared by a process according to claim 64.

73. A compound prepared by a process according to claim 65.

74. A compound prepared by a process according to claim 66.

75. A compound prepared by a process according to claim 67.

76. A compound prepared by a process according to claim 68.

77. A compound prepared by a process according to claim 69.

78. An insecticidal composition comprising a compound according to any one of claims 1—53, 61 or 71, together with a diluent or carrier.

79. A composition according to claim 78 in the form of a dust, a granular solid, wettable powder, mosquito coil, emulsion, emulsifiable concentrate, spray or aerosol.

80. A composition according to claim 78 or 79 containing a pyrethrum synergist.

81. A composition according to any one of claims 78—80 containing pyrethrin or a component thereof or another synthetic pyrethroid.

82. A composition according to any one of claims 78—81 wherein the compound is in accordance with any one of claims 10, 32, 39, 40 or 72.

83. A composition according to any one of claims 78—81 wherein the compound is in accordance with any one of claims 14, 33 or 73.

84. A composition according to any one of claims 78—81 wherein the compound is in accordance with any one of claims 18, 34, 41, 42, 43, 46 or 74.

85. A composition according to any one of claims 78—81 wherein the compound is in accordance with any one of claims 22, 35 or 75.

86. A composition according to any one of claims 78—81 wherein the compound is in accordance with any one of claims 23, 36, 44, 45, 47 or 76.

87. A composition according to any one of claims 78—81 wherein the compound is in accordance with claim 53 or 77.

88. A composition according to any one of claims 78—87 substantially as hereinbefore described.

89. A method of insect control which comprises applying to an insect or to an



environment susceptible to insect attack a compound according to any one of claims 1—53, 61 or 71—77 or a composition according to any one of claims 78—88.

90. A method according to claim 89 wherein the compound is in accordance with any one of claims 10, 32, 39, 40 or 72 or the composition is in accordance with claim 82.

91. A method according to claim 89 wherein the compound is in accordance with any one of claims 14, 33 or 73 or the composition is in accordance with claim 83.

92. A method according to claim 89 wherein the compound is in accordance with any one of claims 18, 34, 41, 42, 43, 46 or 74 or the composition is in accordance with claim 84.

93. A method according to claim 89 wherein the compound is in accordance with any one of claims 22, 35 or 75 or the composition is in accordance with claim 85.

94. A method according to claim 89 wherein the compound is in accordance with any one of claims 23, 36, 44, 45, 47 or 76 or the composition is in accordance with claim 86.

95. A method according to claim 89 wherein the compound is in accordance with claim 53 or 77 or the composition is in accordance with claim 87.

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