Convention Application for a Patent

We, ROUSSEL-UCLAF, a French Body Corporate,

of 35 Boulevard des Invalides, 75007 PARIS, France,

hereby apply for the grant of a Patent

for an invention entitled "PROCESS",

which is described in the accompanying complete specification.

This application is a Convention application and is based on the application numbered 76-12094 for a patent or similar protection made in France, on 23rd April, 1976.

Our address for service is: CALLINAN & NEWTON, Patent Attorneys, of 48-50 Bridge Road, Richmond, State of Victoria, Australia.

Dated this 26th day of April, 1977.

ROUSSEL-UCLAF
By its Patent Attorneys:
CALLINAN AND ASSOCIATES.
AUSTRALIA

Patents Act 1952-1973

Declaration in Support of
(a) A Convention Application
(b) A Non-Convention Application

for a Patent

In support of the Convention Application made by
ROUSSEL-UCLAF

for a patent/Convention Application for an invention entitled:
"PROCESS"

of

XXX Hubert Fritel

35 Boulevard des Invalides, Paris, France

1. (a) I, XXX, Hubert Fritel, declare as follows—
(b) I am/We are authorised by ROUSSEL-UCLAF, the applicant for the patent/Convention Application to make this declaration on its behalf.

2. (i) The basic application, as defined by Section 141 of the Act was made in France on the 23rd day of April 1976 by ROUSSEL-UCLAF.

3. (i) I and/or the actual inventor(s) of the invention

XXX

JULIEN WARNANT of 13, rue Jacques Dulud, NEUILLY-sur-SEINE; JACQUES PROST-MARECHAL of 22, rue Boissy d'Anglas, Paris; and PHILIPPE COSQUER of 73, rue Danielle Casanova, SAINT-DENIS, all of France

are the actual inventor(s) of the invention and the facts upon which the said Company is entitled to make the application are as follows:

(a) The said Company is the assignee of the invention from the said actual inventors.
The compounds find use as insecticides.

CLAIMS

1. Process for converting an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) or a racemic one of structure (R,S) of formula P:

![Chemical Structure](image)

or a mixture, in non-equimolecular proportions, of an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) and an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (S), a mixture denoted by "ester(R + S)" into an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (S), characterised in that the ester of a chiral acid (A) with an
optically-active alcohol (B) of structure (R) or of racemic
structure (R,S), or the mixture of esters called "ester(R + S)"
is subjected to the action of a basic agent selected from the
group constituted by ammonia, the primary amines, the secondary
amines, the tertiary amines, the quaternary ammonium
compounds, the ion exchange resins of basic nature, the
liquid amines of high molecular weight and the strong bases
which, themselves, are used in catalytic amount, in a
solvent or a mixture of solvents in which the ester of a
chiral acid (A) with an alcohol (B) of structure (S) is
insoluble and the ester of a chiral acid (A) with an alcohol
(B) of structure (R) is soluble, then the ester of a chiral
acid (A) with an alcohol (B) of structure (S) thus rendered
insoluble is isolated from the reaction medium.

24. (*S*) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-
dichlorovinyl) cyclopropane-1R-carboxylate.

25. (*R*) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-
dichlorovinyl) cyclopropane-1R-carboxylate.
The following statement is a full description of this invention, including the best method of performing it known to me:

*Note: The description is to be typed in double spacing, pica type face, in an area not exceeding 250 mm in depth and 160 mm in width, on tough white paper of good quality and it is to be inserted inside this form.
The present invention relates to a process for converting a chiral acid ester of an optically-active α-cyano secondary alcohol of structure (R) into a chiral acid ester of an α-cyano secondary alcohol of structure (S).

The subject of the invention is a process for converting a chiral acid ester (A) of optically-active alcohol (B) of structure (I) or a racemic one of structure (R,S), of formula 2:

![Chemical Structure](image)

(R) or (R,S) or a mixture, in non-equimolecular proportions, of chiral acid ester (A) or optically-active alcohol (B) of structure
(R) and ester of a chiral acid (A) with an optically-active alcohol (B) of structure (S), a mixture denoted by "ester (R + S)" into an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (S), characterised in that the ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) or of racemic structure (R,S) or the mixture of esters called "ester(R + S)", is subjected to the action of a basic agent selected from the group constituted by ammonia, the primary amines, the secondary amines, the tertiary amines, the quaternary ammonium compounds, the ion exchange resins of basic nature, the liquid amines of high molecular weight and the strong bases which, themselves, are used in catalytic amount, in a solvent or a mixture of solvents in which the ester of a chiral acid (A) with an alcohol (B) of structure (S) is insoluble and the ester of a chiral acid (A) with an alcohol (B) of structure (R) is soluble, then the ester of a chiral acid (A) with an alcohol (B) of structure (S) thus rendered insoluble is isolated from the reaction medium.

This process will hereinafter be called general process α'.

The subject of the invention is especially a process for converting an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) or a racemic one of structure (R,S) of formula B:
or a mixture, in non-equimolecular proportions, of ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) and ester of a chiral acid (A) with an optically-active alcohol (B) of structure (S), a mixture denoted by "ester (R + S)" into an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (S), characterised in that the ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) or of racemic structure (R,S) or the mixture of esters called "ester (R + S)" is subjected to the action of a basic agent selected from the group constituted by ammonia, the secondary amines, the tertiary amines and the strong bases which, themselves, are used in catalytic amount, in a solvent or a mixture of solvents in which the ester of a chiral acid (A) with an alcohol (B) of structure (S) is insoluble and the ester of a chiral acid (A) with an alcohol (B) of structure (R) is soluble, then the ester of a chiral acid (A) with an alcohol (B) of structure (S) thus rendered insoluble is isolated from
the reaction medium.

This process will hereinafter be called general process $\alpha$.

The chiral acid (A) can be an acid having an asymmetric carbon atom.

The subject of the invention is, therefore, a process according to the general process $\alpha'$ and especially according to the general process $\alpha$ and characterised in that the chiral acid is an acid having an asymmetric carbon atom.

The chiral acid (A) can also be an acid having two asymmetric carbon atoms, especially a cyclopropane carboxylic
acid of which two of the carbon atoms in the ring are asymmetric.

The subject of the invention is, therefore, a process according to the general process \( \alpha \) and especially according to the general process \( \alpha' \), characterized in that the chiral acid (A) is an acid having two asymmetric carbon atoms and more particularly a cyclopropane carboxylic acid of which two of the carbon atoms in the ring are asymmetric carbon atoms.

The chiral cyclopropane carboxylic acid (A) is preferably an optically-active cyclopropane carboxylic acid of cis or trans structure of formula:

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CO}_2\text{H} \\
\text{H}_3\text{C} & \quad \text{H} \\
\text{Hal} & \quad \text{Hal}
\end{align*}
\]

in which Hal represents a chlorine or bromine atom.

Further on in the text, according to a simplified nomenclature adopted recently, the acids of structure \((1R, 3R)\) can be denoted under the name of \((1R, \text{cis})\) acids.

Amongst the preferred chiral cyclopropane carboxylic acids of the invention there will be mentioned especially:

- 2,2-dimethyl \(3R-(2,2\text{-dibromovinyl})\) cyclopropane-1\(R\)-carboxylic acid or 1\(R, \text{cis} 2,2\text{-dimethyl 3(2,2\text{-dibromovinyl}) cyclopropane carboxylic acid, and}

- 2,2-dimethyl \(3R-(2,2\text{-dichlorovinyl})\) cyclopropane-1\(R\)-carboxylic acid or 1\(R, \text{cis} 2,2\text{-dimethyl 3(2,2\text{-dichlorovinyl})}

-4-
cyclopropane carboxylic acid.

The basic agent used in the general process \( \alpha \) of the invention, in the presence of which the conversion of the ester of chiral acid (A) and of optically-active alcohol (B) of structure (R) or the racemic one of structure (R,S) or the mixture, in non-equnolecular proportions, of chiral acid ester (A) of alcohol (B) of structure (R) and of chiral acid ester (A) of alcohol (B) of structure (S) into ester of chiral acid (A) and of alcohol (B) of structure (S) is carried out is preferably selected from the group constituted by ammonia, triethylamine, diethylamine, morpholine, pyrrolidine, piperidine and, used in catalytic amount, sodium hydroxide, potassium hydroxide, the alkali alcoholates, the alkali amides and the alkali hydrides.

This list of bases preferably used in the process \( \alpha \) of the invention is not limiting. Other bases of similar strength could be used without departing from the scope of the invention.

Amongst these bases there may be mentioned those selected from the group constituted by diisopropylamine, ephedrine, triethylendiamine, potassium terbutylate and sodium isopropylate, both these latter bases being used in catalytic amount.

Amongst these basic agents ammonia or triethylamine are used in a particularly advantageous manner.

The basic agent used in the general process \( \alpha' \) of the invention is preferably selected from the group constituted
by ammonia, triethylamine, diethylamine, morpholine, pyrrolidine, piperidine and, used in catalytic amount, sodium hydroxide, potassium hydroxide, the alkali alcoholates, the alkali amides and the alkali hydrides.

This list of bases preferably used in the process of the invention is not limiting. Other bases of similar strength could be used without departing from the scope of the invention.

Amongst these bases there may be mentioned those selected from the group constituted by diisopropylamine, ephedrine, triethylenediamine potassium terbutylate and sodium isopropylate, both these latter bases being used in catalytic amount.

As basic agent according to the general process α' benzylamine, n-butylamine, sec-butylamine and tetrabutyl ammonium hydroxide can also be used.

The basic agent used can also be an ion exchange resin of strong basic nature containing quaternary ammonium compounds or amines.

The DOW chemical company sells such basic agents under the name "DOWEX" and the company ROHM and HAAS sells similar basic agents under the name "AMBERLITE". These commercial products are advantageously used as basic agents in the process α' of the invention.

For example DOWEX AGIX8 or AMBERLITE IRA 400 or IR 45 can be used.

The basic agent used can also be an amine of high molecular weight insoluble in water.
The company ROHM and HAAS sells, under the name of "liquid AMBERLITE", products which can advantageously be employed as basic agents according to the process $\alpha'$ of the invention.

Thus it is that LIQUID AMBERLITES of type LAl or LA2 can be used.

The solvent or the mixture of solvents used in the process $\alpha'$ and especially in the process $\alpha$ is advantageously selected from the group constituted by acetonitrile, the alkanols and the mixtures of alkanol and petroleum ether, especially the mixtures of alkanol and pentane, hexane or heptane and more particularly from the group constituted by acetonitrile, propanol, isopropanol, the straight and branched butanols and by the mixtures of the above alcohols with "essence G", "essence B", "essence C", "essence E", pentane, hexane or heptane.

Isopropanol is particularly interesting for carrying out the conversion according to the processes of the invention.

It is quite obvious that the terms "insoluble" for the alcohol esters of structure (S) and "soluble" for the alcohol esters of structure (R) are used in their current meaning. In the solvents used according to the processes of the invention the alcohol esters of structure (S) show a certain solubility which must be sufficiently slight for the yield to be good, considering the volume of solvent used. In practice, the solvents or mixture of solvents used as well as the volumes of these solvents employed
enable a yield by weight of alcohol ester of structure (S) of at least 80% to be obtained. The list of solvents or mixture of solvents mentioned above is not by way of limitation. Other solvents or mixture of solvents could be used without departing from the scope of the invention.

The alcohol esters of structure (R) are generally very soluble in the solvents used according to the processes of the invention and a limited volume of solvent enables them to be dissolved totally.

The reaction temperature influences the speed of the reaction.

The reaction period depends especially upon the temperature and also upon the nature of the base used.

Amongst the chiral acids (A) of the cyclopropane carboxylic type one of the more particularly preferred acids of the invention is 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane 1R-carboxylic acid or 1R,cis 2,2-dimethyl 3-(2,2-dibromovinyl) cyclopropane carboxylic acid.

The invention therefore relates to a process according to the general process (α') for converting a 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylic acid and ester of optically-active α-cyano 3-phenoxybenzyl alcohol of structure (R) or a racemic one of structure (R,S) of formula (B):

![Chemical Structure](image)

(R) or (R,S)
or a mixture, in non-equimolecular proportions, of (R) \( \alpha \)-

-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl)
cyclopropane-1R-carboxylate and (S) \( \alpha \)-cyano 3-phenoxybenzyl
2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, a
mixture denoted by "dibromo (R + S) ester" into (S) \( \alpha \)-cyano
3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclo-

propane-1R-carboxylate, characterized in that the optically-active
alcohol ester of structure (R), the racemic alcohol ester of structure
(R,S) or the mixture called "dibromo (R + S) ester", defined above, is
subjected to the action of a basic agent selected from the group
constituted by ammonia, the primary amines, the secondary amines, the
tertiary amines, the quaternary ammonium compounds, the
ion exchange resins of basic nature, the liquid amines of high
molecular weight and the strong bases which, themselves, are
used in catalytic amount in a solvent or a mixture of
solvents in which (S) \( \alpha \)-cyano 3-phenoxybenzyl 2,2-dimethyl
3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate is
insoluble and in which (R) \( \alpha \)-cyano 3-phenoxybenzyl 2,2-
dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate
is soluble, then the alcohol ester of structure (S) thus
rendered insoluble is isolated from the reaction medium,
this being called process \( \beta ' \).

The invention relates especially to a process according
to the general process (\( \alpha \)) for converting an ester of
2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylic
acid of optically-active \( \alpha \)-cyano 3-phenoxybenzyl alcohol
of structure (R) or a racemic one of structure (R,S) of formula (B):

![Chemical Structure](image)

(R) or (R,S)

or a mixture, in non-equimolecular proportions, of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate and (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, a mixture denoted by "dibromo(R+S) ester" into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate characterized in that the optically-active alcohol ester of structure (R), the racemic alcohol ester of structure (R,S) or the mixture called "dibromo(R+S) ester", defined above, is subjected to the action of a basic agent selected from the group constituted by ammonia, the secondary amines, the tertiary amines and the strong bases which, themselves, are used in catalytic amount in a solvent or a mixture of solvents in which the (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate is insoluble and in which the (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate is soluble, then the alcohol ester of structure (S) thus rendered insoluble is isolated from the reaction medium, this being called process β.
In order to carry out the conversion of optically-active alcohol ester of structure (R) of racemic alcohol ester (R,S) or of the mixture, in non-equimolecular proportions, of optically-active alcohol esters into optically-active alcohol ester of structure (S) according to the process β' and especially the process β, described above, the basic agent and the solvent or the mixture of solvents preferably used are identical to the basic agents and solvents mentioned above for the processes α' and α.

The subject of the invention is more especially a process according to the process β for converting (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, characterized in that the optically-active alcohol ester of structure (R) is subjected to the action of a basic agent selected from the group constituted by ammonia, the secondary amines, the tertiary amines and the strong bases which, themselves, are used in catalytic amount, in a solvent selected from the group constituted by acetonitrile, the alcohols and the mixtures of alkanol and petroleum ether, especially the mixtures of alkanol and pentane, hexane or heptane, called process γ and more particularly a process according to the process γ in which the basic agent is ammonia or triethylamine and the solvent is isopropanol.

The subject of the invention is also a process according to the process β', characterized in that the conversion is carried out starting with the optically-active
alcohol ester of structure (R), a process called \( \gamma' \).

The subject of the invention is more especially a process according to the process \( \beta \) for converting \((R,S)\) \(\alpha\)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into \((S)\) \(\alpha\)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, characterized in that the racemic alcohol ester is subjected to the action of a basic agent selected from the group constituted by ammonia, the secondary amines, the tertiary amines and the strong bases which, themselves, are used in catalytic amount in a solvent selected from the group constituted by acetonitrile, the alkanols and the mixtures of alkanol and petroleum ether especially the mixtures of alkanol and pentane, hexane or heptane, called process \( \delta \) and especially a process according to the process \( \delta \) in which the basic agent is ammonia or triethylamine and the solvent is isopropanol.

The subject of the invention is also a process according to the process \( \beta' \), characterized in that the conversion is carried out starting with the racemic alcohol ester, a process called \( \delta' \).

The invention also aims at a process according to the process \( \beta \) for converting a mixture, in non-equimolecular proportions, of \((R)\) \(\alpha\)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate and \((S)\) \(\alpha\)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, characterized in that the mixture of esters is subjected to the action of a basic
cyclopropane-LR-carboxylate, into (S) α-cyano 3-phenoxybenzyl
2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-LR-carboxylate,
characterised in that the mixture of esters is subjected to
the action of a basic
agent selected from the group constituted by ammonia, the secondary amines, the tertiary amines and the strong bases which, themselves, are used in catalytic amount, in a solvent selected from the group constituted by acetonitrile, the alkanols and the mixtures of alkanol and petroleum ether especially the mixtures of alkanol and pentane, hexane or heptane, called process ε and more particularly a process according to the process ε characterized in that the basic agent is ammonia or triethylamine and the solvent is isopropanol.

The subject of the invention is also a process according to the process β', characterized in that the conversion is carried out starting with the mixture called "dibromo(R + S) ester", a process called ε'.

The subject of the invention is also a process according to the process α for converting a 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylic acid ester of optically-active α-cyano 3-phenoxybenzyl alcohol of structure (R) or the racemic one of structure (R,S) of formula:

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\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\includegraphics[width=0.5\textwidth]{formula.png}};
\end{tikzpicture}
\end{center}
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or a mixture, in non-equimolecular proportions, of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate and (S) α-cyano 3-phenoxybenzyl
2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate, a mixture denoted by "dichloro(R + S) ester" into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate, characterized in that the optically-active alcohol ester of structure (R), the racemic alcohol ester (R,S) of the mixture called "dichloro(R + S) ester" is subjected to the action of a basic agent selected from the group constituted by ammonia, the secondary amines, the tertiary amines and the strong bases which, themselves, are used in catalytic amount, in a solvent or a mixture of solvents in which the (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate is insoluble and in which the (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate is soluble, then the alcohol ester of structure (S) thus rendered insoluble is isolated from the reaction mixture, this being called process β₁.

The subject of the invention is also a process according to the process α', characterized in that the chiral acid (A) is 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylic acid, a process called β₁'.

The basic agent and the solvent or the mixture of solvents preferably used in the process β₁ and especially the process β₁ are identical to the basic agents and solvents mentioned above for the processes α' and α.

The subject of the invention is also a process according to the process β₁ for converting (R) α-cyano...
3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate, characterized in that the optically-active alcohol ester of structure (R) is subjected to the action of a basic agent selected from the group constituted by ammonia, the secondary amines, the tertiary amine, and the strong bases which, themselves, are used in catalytic amount, in a solvent selected from the group constituted by acetonitrile, the alkanols and the mixtures of alkanol and petroleum ether especially the mixtures of alkanol and pentane, hexane or heptane, this being called process γ_1.

In a preferred method of carrying out the process γ_1 the basic agent is ammonia or triethylamine and the solvent is isopropanol.

The subject of the invention is also a process according to the process B'_1, characterized in that the conversion is carried out starting with the optically-active alcohol ester of structure (R), a process called β'_1.

The invention also relates to a process according to the process B'_1 for converting (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate, characterized in that the racemic alcohol ester (R,S) is subjected to the action of a basic agent selected from the group constituted by ammonia, the secondary amines, the tertiary amines and the strong bases which, themselves, are
used in catalytic amount, in an organic solvent selected from the group constituted by acetonitrile, the alkanols and the mixtures of alkanol and petroleum ether especially the mixtures of alkanol and pentane, hexane or heptane, this being called process $\beta_1$.

In a preferred method of carrying out the process $\beta_1$ the basic agent is ammonia or triethylamine and the solvent used is isopropanol.

The subject of the invention is also a process according to the process $\beta'_1$, characterized in that the conversion is carried out starting with the racemic alcohol ester $(R, S)$, a process called $\delta'_1$.

The invention also relates to a process according to the process $\beta_1$ for converting a mixture, in non-equimolecular proportions, of $(R)$ $\alpha$-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate and $(S)$ $\alpha$-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate into $(S)$ $\alpha$-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate, a mixture denoted by "dichloro$(R + S)$ ester", characterized in that the mixture of esters is subjected to the action of a basic agent selected from the group constituted by ammonia, the secondary amines, the tertiary amines and the strong bases which, themselves, are used in catalytic amount, in an organic solvent selected from the group constituted by acetonitrile, the alkanols and the mixtures of alkanol and petroleum ether especially the
mixtures of alkanol and pentane, hexane or heptane, a process called process $s_1$.

In a preferred method of carrying out the process $s_1$ the basic agent is ammonia or triethylamine and the solvent is isopropanol.

The subject of the invention is also a process according to the process $s'_1$, characterized in that the conversion is carried out starting with the mixture called "dichloro($R+S$) ester", a process called $s'_1$.

It is possible to give for the working of the process of the invention the following explanation:

By the action of a base of suitable strength and which, in practice, is selected from the group constituted by ammonia, the primary amines, the secondary amines, the tertiary amines, the quaternary ammonium compounds, the ion exchange resins of basic nature, the liquid amines of high molecular weight and the strong bases used in catalytic amount, the chiral acid ester (A) of optically-active alcohol of structure (K) contained in the starting product gives rise to an $\alpha$-cyano carbamion which causes racemisation of the corresponding carbon atom.

Subsequent protonation in a solvent or a mixture of solvents then leads, for the soluble fraction, to the formation, in equimolecular proportions, of the two diastereoisomers [(S) alcohol ester and (R) alcohol ester] according to the diagram:
In the solvent or the mixture of solvents, used according to the process of the invention the acid ester (A) and of alcohol (B) of structure (S) being insoluble and the ester of acid ester (A) of alcohol (B) of structure (R) being soluble, the equilibrium is then displaced towards the formation of the alcohol ester (B) of structure (S) resulting, in practice, in yields of alcohol ester (B) of structure (S) of 80 to 90% with reference to the optically-active starting ester employed.
The intermediate formation of the mixture of alcohol ester (S) and alcohol ester (R) in equimolecular proportions can be made evident by evaporating the soluble fraction to dryness. The racemisation process takes place with a practically quantitative yield when, contrary to the case of the present invention, a solvent or a mixture of solvents is used in which the alcohol ester (S), the alcohol ester (R) and the racemic alcohol ester are soluble, and forms the subject of a Patent Application filed on the same day (Case 1736), under the title "Process for converting a chiral acid ester of optically-active α-cyano secondary alcohol into a chiral acid ester of racemic α-cyano secondary alcohol".

This theoretical explanation of the process of the invention, although it gives an account of all the facts observed obviously is only given for guidance and in no way limits the scope of the invention.

The process of the invention is of a particularly unexpected nature, for there did not exist until then, as far as is known, any process for converting an optically-
active alcohol ester into an optically-active alcohol ester of antipodal structure with an almost quantitative yield.

The process of the invention is particularly interesting when the chiral acids used are the optically-active cyclopropane carboxylic acids of structure 1R,3R (or 1R,cis), of formula:

\[
\begin{align*}
 & H_2C \\
 & H_3C \\
 & COOH
\end{align*}
\]

\[
\begin{align*}
 & Z \\
 & Z
\end{align*}
\]

in which Z represents a bromine atom or a chlorine atom.

In fact for several years insecticidal compounds endowed with exceptionally high activity have been prepared by esterifying the chiral acids mentioned above with \(\alpha\)-cyano 3-phenoxybenzyl alcohol.

Moreover it has been proved, generally speaking, that the chiral acid esters above of optically-active \(\alpha\)-cyano 3-phenoxybenzyl alcohol of structure (S) possess insecticidal activity which is much higher than the corresponding esters of racemic (R,S) or optically-active alcohol of structure (R).

Now \(\alpha\)-cyano 3-phenoxybenzyl alcohol is obtained by synthetic route in the form of a racemic compound. The weakness of its molecule, moreover, does not permit stereo selective preparation of the enantiomeres, nor resolution of the racemic alcohol to be considered.

In order to obtain the alcohol esters of structure (S) of the cyclopropane carboxylic acids mentioned above having a dibromo or dichlorovinyl chain, the only process known to
date consisted in carrying out a separation of the alcohol ester of structure (R) and of the alcohol ester of structure (S) by selectively rendering the latter insoluble in a suitable solvent which led to a mediocre yield necessarily below 50% with reference to the racemic ester used.

The alcohol ester (R) or the mixtures of alcohol ester (R) and of alcohol ester (S) rich in alcohol ester (R) thus resulting from the preparation of the alcohol ester (S) thus appeared to be not easily recoverable residues from the preparation of the alcohol esters (S).

The process of the present invention now permits direct conversion with an almost quantitative yield either of the 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylic acid esters or the 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylic acid esters of racemic α-cyano 3-phenoxybenzyl alcohol of structure R,S or of the alcohol esters of structure (R) of these acids, or of mixtures of alcohol esters of structure (R) and alcohol esters of structure (S), in non-equimolecular proportion, and especially the mixtures of esters rich in alcohol ester (R) into alcohol ester of structure (S) with an almost quantitative yield.

The process of the invention comprising only one stage, employing simple working and using not very extensive reagents enables there to be obtained with a very high yield under particularly advantageous conditions the cyclopropane carboxylic acid esters mentioned above containing a dichloro or dibromovinyl chain of optically-active α-cyano 3-phenoxybenzyl alcohol of structure (S),
which esters have exceptionally high insecticidal activity.

(S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate and (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate are not described in the literature.

These compounds form part of the invention.

The first of these compounds, that is to say the alcohol ester (S) is particularly suitable for use in controlling insects in the agricultural sphere.

For example, it permits effective control of aphids, the larvae of Lepidoptera, and Coleoptera. It can also be used as an insecticide in the domestic field (flies, mosquitoes).

Tests given in the experimental portion show the separate insecticidal activity of this compound with respect to the domestic fly and against the larvae of Spodoptera littoralis.

(R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate is endowed with an insecticidal activity which is less intense than that of the corresponding alcohol ester (S).

The subject of the invention is also insecticidal compositions containing, as active principle, (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate and those which contain, as active principle, (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate.

In those compositions the active material can be mixed with one or more other pesticidal agents.
These compositions can be presented in the form of powders, granules, suspensions, emulsions, solutions, solutions for aerosols, combustible strips, baits or other preparations normally employed for the use of this kind of compound.

In addition to the active principle these compositions generally contain a vehicle and/or a non-ionic surface-active agent ensuring, in addition, uniform dispersion of the substances constituting the mixture. The vehicle used can be a liquid such as water, alcohol, the hydrocarbons or other organic solvents, a mineral, animal or vegetable oil, a powder such as talc, the clays, the silicates or kieselguhr or a combustible solid such as tabu powder (or pyrethrum marc).

In order to increase the insecticidal activity of the two compounds mentioned above they can be mixed with the standard synergists used in similar cases such as 1(2,5,8-trioxo dodecyl 2-propyl 4,5-methylenedioxy) benzene (or piperonyl butoxide), N-(2-ethylheptyl) bicyclo [2,2,1]-5-heptene-2,3-dicarboximide, and piperonyl-bis-2-(2'-n-butoxy ethoxy) ethyl acetal (or tropital).

These insecticidal compositions preferably contain between 0.005% and 10% by weight of active material.

The following Examples illustrate the invention without limiting it.
Example 1: Conversion of (R) \( \alpha \)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) \( \alpha \)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Into 2.5 cm\(^3\) of isopropanol one introduces 1 g of (R) \( \alpha \)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, \([\alpha]_D^{20} = -30.5^\circ\) (c = 1%, benzene) or \([\alpha]_D^{20} = -25.5^\circ\) (c = 1%, chloroform), then 0.15 cm\(^3\) of aqueous solution of 22\(^\circ\) Bé ammonia, agitates for eighteen hours at 20\(^\circ\)C, isolates by vacuum-filtration the precipitate formed, washes its, dries it and obtains 0.9 g of (S) \( \alpha \)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, M.Pt. = 100\(^\circ\)C, \([\alpha]_D^{20} = +60.5^\circ\) (c = 1%, benzene), \([\alpha]_D^{20} = +25^\circ\) (c = 1%, chloroform).

Analysis \( C_{22}H_{19}O_3NBr_2 \) (502.2)

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Example 2: Conversion of (R) \( \alpha \)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropene-1R-carboxylate into (S) \( \alpha \)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Starting with 1 g of alcohol ester (R), operating in a manner similar to that of Example 1 but using 0.30 cm\(^3\) of aqueous solution of 22\(^\circ\) Bé ammonia, one obtains 0.9 g of alcohol ester (S) of the same quality as in Example 1.

Example 3: Conversion of (R) \( \alpha \)-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-
carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Starting with 1 g of alcohol ester (R), using a modus operandi similar to that of Example 1 but replacing the ammonia with 0.16 g of triethylamine, one obtains 0.87 g of alcohol ester (S) of the same quality as in Example 1.

Example 4: Conversion of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Starting with 1 g of alcohol ester (R), using a modus operandi similar to that of Example 1 but replacing the ammonia with 0.32 g of triethylamine, one obtains 0.9 g of alcohol ester (S) of the same quality as in Example 1.

Example 5: Conversion of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Starting with 1 g of alcohol ester (R), using a modus operandi similar to that of Example 1 but replacing the ammonia with 0.11 g of pyrrolidine, one obtains 0.80 g of alcohol ester (S) of the same quality as in Example 1.

Example 6: Conversion of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Starting with 1 g of alcohol ester (R), using a modus operandi similar to that of Example 1 but replacing the ammonia with 0.13 g of morpholine and agitating for ninety
-six hours at 20°C, one obtains 0.9 g of alcohol ester (S) of the same quality as in Example 1.

**Example 7:** Conversion of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Starting with 1 g of alcohol ester (R), using a modus operandi similar to that of Example 1 but replacing the ammonia with 0.008 g of sodium hydroxide, one obtains 0.85 g of alcohol ester (S) of the same quality as in Example 1.

**Example 8:** Conversion of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Starting with 1 g of alcohol ester (R), operating in a manner similar to that of Example 1 but replacing the 2.5 cm³ of isopropanol with 2.5 cm³ of butanol, one obtains 0.80 g of alcohol ester (S) of the same quality as in Example 1.

**Example 9:** Conversion of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Starting with 1 g of alcohol ester (R), operating in a manner similar to that of Example 1 but replacing the 2.5 cm³ of isopropanol with 2.5 cm³ of terbutanol, one obtains 0.85 g of alcohol ester (S) of the same quality as in Example 1.
Example 10: Conversion of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

In a mixture of 2 cm$^3$ of acetonitrile and 0.5 cm$^3$ of water one dissolves 1 g of alcohol ester (R), adds 0.15 cm$^3$ of aqueous solution of 22° Bé ammonia, agitates for eighteen hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with acetonitrile containing 25% of water, dries it and obtains 0.87 g of alcohol ester (S) of the same quality as in Example 1.

Example 11: Conversion of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Starting with 1 g of alcohol ester (R), using the same modus operandi as in Example 9, using 2.5 cm$^3$ of terbutanol but replacing the ammonia with 0.16 g of triethylamine, one obtains 0.8 g of alcohol ester (S) of the same quality as in Example 1.

Example 12: Conversion of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Starting with 1 g of alcohol ester (R), using the same modus operandi as in Example 8 using 2.5 cm$^3$ of butanol but replacing the ammonia with 0.11 g of pyrrolidine, one obtains 0.8 g of alcohol ester (S) of the same quality.
as in Example 1.

Example 13: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

105 g of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, [α]_D^0 = 0° to -1° (c = 1%, chloroform) and [α]_D^0 = +14° (c = 1%, benzene), are dissolved in 262.5 cm^3 of isopropanol.

To the solution one adds 15 cm^3 of aqueous solution of 22° Bé ammonia, agitates for eighteen hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with 105 cm^3 of isopropanol, dries it and obtains 95.1 g of (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate. M.P. = 100°C, [α]_D^20 = +60.5° (c = 1%, benzene) of the same quality as in Example 1.

Example 14: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Into 2.5 cm^3 of isopropanol one introduces 1 g of racemic alcohol ester (R,S), adds 0.30 cm^3 of aqueous solution of 22° Bé ammonia, agitates for twenty hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with 1 cm^3 of isopropanol, dries it and obtains 0.9 g of alcohol ester (S) of the same quality as in Example 1.
Example 15: Conversion of (R,S) \(\alpha\)-cyano 3-phenoxycarbonyl
2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-lR-
carboxylate into (S) \(\alpha\)-cyano 3-phenoxycarbonyl 2,2-dimethyl
3R-(2,2-dibromovinyl) cyclopropane-lR-carboxylate.

Into 2.5 cm\(^3\) of isopropanol one introduces 1 g of racemic alcohol ester (R,S), adds 0.16 g of triethylamine, agitates for fifteen hours at 20\(^\circ\)C, isolates by vacuum-filtration the precipitate formed, washes it with 1 cm\(^3\) of isopropanol, dries it and obtains 0.87 g of alcohol ester (S) of the same quality as in Example 1.

Example 16: Conversion of (R,S) \(\alpha\)-cyano 3-phenoxycarbonyl
2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-lR-
carboxylate into (S) \(\alpha\)-cyano 3-phenoxycarbonyl 2,2-dimethyl
3R-(2,2-dibromovinyl) cyclopropane-lR-carboxylate.

Into 2.5 cm\(^3\) of isopropanol one introduces 1 g of racemic alcohol ester (R,S), adds 0.32 g of triethylamine, agitates for fifteen hours at 20\(^\circ\)C, isolates by vacuum-filtration the precipitate formed, washes it with 1 cm\(^3\) of isopropanol, dries it and obtains 0.9 g of alcohol ester (S) of the same quality as in Example 1.

Example 17: Conversion of (R,S) \(\alpha\)-cyano 3-phenoxycarbonyl
2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-lR-
carboxylate into (S) \(\alpha\)-cyano 3-phenoxycarbonyl 2,2-dimethyl
3R-(2,2-dibromovinyl) cyclopropane-lR-carboxylate.

Into 2.5 cm\(^3\) of isopropanol one introduces 1 g of racemic alcohol ester (R,S), adds 0.13 g of morpholine, agitates for ninety-six hours at 20\(^\circ\)C, isolates by vacuum-filtration the precipitate formed, washes it with 1 cm\(^3\) of isopropanol, dries it and obtains 0.9 g of alcohol
ester (S) of the same quality as in Example 1.

Example 18: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3E-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

Into 2.5 cm$^3$ of isopropanol one introduces 1 g of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, adds 0.008 g of sodium hydroxide, agitates for eighteen hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with 1 cm$^3$ of isopropanol, dries it and obtains 0.85 g of alcohol ester (S) of the same quality as in Example 1.

Example 19: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3E-(2,2-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

One dissolves 1 g of racemic alcohol ester (R,S) in a mixture of 2 cm$^3$ of acetonitrile and 0.5 cm$^3$ of water, adds 0.15 cm$^3$ of aqueous solution of 22° Bé ammonia, agitates for seventeen hours at 70°C, isolates by vacuum-filtration the precipitate formed, washes it with acetonitrile containing 25% of water, dries it and obtains 0.87 g of alcohol ester (S) of the same quality as in Example 1.

Example 20: Conversion of a mixture of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate and (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate containing more than 50% by weight of alcohol ester (R).
a) Preparation of the mixture of alcohol (R) and alcohol (S) esters:

One introduces 10 g of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, [α]_D^{20} = 0°, -1° (c = 1%, chloroform) and [α]_D^{20} = +14° (c = 1%, benzene), into 20 cm³ of isopropanol, agitates for eighteen hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with 10 cm³ of isopropanol, dries it and obtains 4 g of alcohol ester (R). M.Pt. = 100°C, [α]_D^{20} = +60°C (c = 1%, benzene).

One reunites the filtrate and the washing liquors and obtains a solution (solution L) which contains 5 g of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate and 1 g of (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

b) Conversion of the mixture of alcohol ester (R) and alcohol ester (S) into alcohol ester (S):

To the solution L one adds 0.8 cm³ of aqueous solution of 22° Bé ammonia, agitates for twenty hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with 5 cm³ of isopropanol, dries it and obtains 4.5 g of (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate. M.Pt. = 100°C, [α]_D^{20} = +60°C (c = 1%, benzene) of the same quality as in Example 1 or 13.

Example 21: Conversion of (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate.
a) Preparation of the alcohol ester of structure (R):

10 g of racemic alcohol ester (R,S) of $[\alpha]_{D}^{20} = +16.5^\circ$ ($\alpha = 10\%$, benzene) are chromatographed on silica gel eluting with a mixture of petroleum ether (B.Pt. 40° - 70°C) and isopropyl ether (85:15), and one obtains 3 g of (R) $\alpha$-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate of $[\alpha]_{D}^{20} = -31^\circ$ ($\alpha = 1\%$, benzene) or $[\alpha]_{D}^{20} = -21.5^\circ$ ($\alpha = 1\%$, chloroform).

b) Conversion into alcohol ester of structure (S):

To 60 g of (R) $\alpha$-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate $[\alpha]_{D}^{20} = -31^\circ$ ($\alpha = 1\%$, benzene) or $[\alpha]_{D}^{20} = -21.5^\circ$ ($\alpha = 1\%$, chloroform) obtained in paragraph a) one adds 120 cm$^3$ of isopropanol then 9 cm$^3$ of aqueous solution of 22° Bé ammonia, cools to 0°C, agitates for forty-eight hours at 0°C, isolates by vacuum-filtration the precipitate formed, washes it with 30 cm$^3$ of isopropanol at -20°C, dries it and obtains 48.5 g of (S) $\alpha$-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate. M.Pt. = 60°C, $[\alpha]_{D}^{20} = +65^\circ$ ($\alpha = 1\%$, benzene) or $[\alpha]_{D}^{20} = +34^\circ$ ($\alpha = 1\%$, chloroform).

Example 22: Conversion of (R,S) $\alpha$-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate into (S) $\alpha$-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate.

To 600 g of racemic alcohol ester (R,S), $[\alpha]_{D}^{20} = +16.5^\circ$ ($\alpha = 10\%$, benzene) one adds 1200 cm$^3$ of isopropanol, then introduces into the solution obtained 90 cm$^3$ of aqueous solution of 22° Bé ammonia, cools to 0°C, agitates for
forty-eight hours at this temperature, isolates by vacuum-filtration the precipitate formed, washes it with 300 cm$^3$ of isopropanol at -20$^\circ$C, dries it and obtains 485 g of (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate. M.Pt. = 60$^\circ$C, $[\alpha]_D^{20} = +66^\circ$ (c = 1%, benzene) or $[\alpha]_D^{20} = +34^\circ$ (c = 1%, chloroform).

**Analysis:** $C_{22}H_{19}O_2NCl_2$ (416.28)

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**Example 23:** Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One dissolves 10 g of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate $[\alpha]_D^{20} = 0^\circ$ to -1$^\circ$ (c = 1%, chloroform) and $[\alpha]_D^{20} = +14^\circ$ (c = 1%, benzene) in 25 cm$^3$ of isopropanol, adds 0.8 g of diisopropylamine, agitates for six hours at 20$^\circ$C then two hours at 0$^\circ$C, isolates by vacuum-filtration the precipitate formed, crystallises it in two volumes of isopropanol and obtains 8.04 g of (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate $[\alpha]_D^{20} = +57^\circ$ (c = 4%, toluene).

**Example 24:** Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.
One operates in a manner similar to that of Example 23 but agitating for forty-eight hours at 0°C and obtains the same yield of product of the same quality as in Example 23.

Example 25: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2′,2′-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2′,2′-dibromovinyl) cyclopropane-1R-carboxylate.

One operates in a manner similar to that of Example 23 but replacing the isopropanol with isopropanol containing 3.5% of water, agitating for eight hours at 20°C and one obtains 8.16 g of (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2′,2′-dibromovinyl) cyclopropane-1R-carboxylate [α]D20 = +56.5° (c = 4%, toluene).

Example 26: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2′,2′-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2′,2′-dibromovinyl) cyclopropane-1R-carboxylate.

One dissolves 10 g of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2′,2′-dibromovinyl) cyclopropane-1R-carboxylate, [α]D20 = 0° to -1° (c = 1%, chloroform) and [α]D20 = +14° (c = 1%, benzene), in 25 cm3 of isopropanol, adds 1.39 g of piperidine, agitates for eighteen hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with isopropanol, dries it and obtains 8.6 g of (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2′,2′-dibromovinyl)cyclopropane-carboxylate identical to the product obtained in Examples 23 to 25.
Example 27: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One operates in a manner similar to that of Example 26 but replacing the 1.39 g of piperidine with 1.66 g of diisopropylamine and obtains, starting with 10 g of alcohol ester (R,S), 8.85 g of alcohol ester (S) of the same quality as in Examples 23 to 26.

Example 28: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One operates in a manner similar to that of Example 26 but replacing the 1.39 g of piperidine with 2.7 g of ephedrine, agitating for twenty-four hours at 20°C, and one obtains, starting with 10 g of alcohol ester (R,S), 8.7 g of alcohol ester (S) of the same quality as in Examples 23 to 27.

Example 29: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One operates in a manner similar to that of Example 23 but replacing the 0.8 g of diisopropylamine with 4.4 g of triethylenediamine (or 2,4-P.C.O.) and one obtains, after seventy-two hours' agitation at 20°C, 7.5 g of alcohol ester (S) of the same quality as those obtained in Examples 23 to 28.
Example 30: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One dissolves 10 g of alcohol ester (R,S) in 25 cm$^3$ of isopropanol, adds 0.23 g of potassium terbutylate, agitates for eighteen hours at 20°C and obtains 7.7 g of alcohol ester (S) of the same quality as in Examples 23 to 29.

Example 31: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One operates in a manner similar to that of Example 30 replacing the 0.23 g of potassium terbutylate with 0.34 g of sodium isopropylate, agitating for twenty-four hours at 20°C, and one obtains 7.3 g of alcohol ester (S) of the same quality as in Examples 23 to 30.

Example 32: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One dissolves 10 g of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate, $[\alpha]_{D}^{20} = 0^0$ to $1^0$ (c = 1%, chloroform) and $[\alpha]_{D}^{20} = +14^0$ (c = 1%, benzene), in 25 cm$^3$ of isopropanol containing 3.5% of water, adds 0.84 g of benzylamine,
agitates for twenty-three hours at 20°C, isolates by vacuum-filtration the precipitate formed, crystallises it in two volumes of isopropanol and obtains 8.25 g of (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate, [α]_D^20 = +57° (c = 4%, toluene).

Example 33: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One dissolves 10 g of alcohol ester (R,S) in 25 cm³ of isopropanol, adds 1.20 g of n-butylamine, agitates for twenty-four hours at 20°C, isolates by vacuum-filtration the precipitate formed, and obtains 9.0 g of alcohol ester (S) of the same quality as in Examples 23 to 32.

Example 34: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

Operating in a manner similar to that of Example 32 but using 1.20 g of sec-butylamine (or 1-methyl propylamine), agitating for twenty-four hours at 20°C, one obtains 9.1 g of alcohol ester (S) of the same quality as in Examples 23 to 32.

Example 35: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl...
3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

Operating in a manner similar to that of Example 30 but replacing the 0.23 g of potassium terbutylate with 0.64 cm$^3$ of 40% aqueous solution of tetrabutyl ammonium hydroxide, one obtains, after twenty-four hours' agitation at 20°C, 8.4 g of alcohol ester (8) of the same quality as in Examples 23 to 34.

Example 36: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One dissolves 10 g of alcohol ester (R,S) in 25 cm$^3$ of iso-propanol, adds 10 g of AMBERLITE IRA 400 resin (mesh size 20/50; and which is a strongly basic styrene and divinyl benzene copolymer containing quaternary ammonium functions), previously washed with perchloric acid diluted to 1/3, with water until neutral, with NaOH solution, then with water, one agitates for twenty-four hours at 20°C, isolates by vacuum-filtration the precipitate (mixture of resin and alcohol ester (S) ), adds methylene chloride thereto, agitates, filters, concentrates the filtrate to dryness and obtains 7.8 g of alcohol ester (S) of the same quality as in Examples 23 to 35.

Example 37: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.
One operates in a manner similar to that of Example 36 but using 10 g of AMBERLITE IR45 resin (of mesh size 20/50; and which is a slight/basic styrene and divinyl benzene copolymer containing primary, secondary and tertiary amine groups) and obtains, after seventy-two hours' agitation at 20°C, 8.1 g of alcohol ester (S) of identical quality to the products obtained in Examples 23 to 36.

**Example 38**: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One operates in a manner similar to that of Example 36 but using 10 g of DOWEX AG1X8 resin (mesh size 200/400; and which is an anion exchanger of strong basic nature of which the active group is a trimethyl benzyl ammonium group, the product containing 8% of divinyl benzene), and obtains, after seventy-two hours' agitation at 20°C, 7 g of alcohol ester (S) of quality identical to that of the products obtained in Examples 23 to 37.

**Example 39**: Conversion of (R,S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One operates in a manner similar to that of Example 36 but using 10 g of liquid AMBERLITE LAI (amines of high molecular weight by the company ROHM and HAAS, of viscosity 72 cps at 25°C) and after seventy-two hours' agitation.
obtains 8.9 g of alcohol ester (S) of the same quality as the products obtained in Examples 23 to 38.

Example 40: Conversion of (R,S) α-cyano 3-phenox ybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenox ybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One operates in a manner similar to that of Example 36 but using 3.75 g of liquid AMBERLITE LA2 of viscosity 18 cps at 25°C and after eighteen hours' agitation at 20°C obtains 8.1 g of alcohol ester (S) of identical quality to that of the products obtained in Examples 23 to 39.

Example 41: Conversion of (R,S) α-cyano 3-phenox ybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate into (S) α-cyano 3-phenox ybenzyl 2,2-dimethyl 3R-(2',2'-dibromovinyl) cyclopropane-1R-carboxylate.

One proceeds in a manner similar to that of Example 26 but replacing the isopropanol with isopropanol containing 3.5% of water, and obtains, by agitating for twenty-four hours at 20°C, 8.95 g of alcohol ester (S) of the same quality as that obtained in Examples 23 to 40.

Example 42: Composition based upon (S) α-cyano 3-phenox ybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate.

One mixes:

-(S) α-cyano 3-phenox ybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate ............... 25 g/l
-2,6-diterbutyl para cresol ................. 10 g/l
-EMCOL II 3GU 1* ......................... 50 g/l
These surface-active agents are mixtures of calcium salts of alkyl benzene sulphonates (anionic portion) and polyoxyethylenated ethers (non-ionic portion), sold by the company WITE.

**Supersol** is a mixture of aromatic solvents sold by the company B.F. (SHELL).

Study of the insecticidal activity of \((s)\) \(-\text{cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate (Compound A).}\)

A - Study of the insecticidal activity with respect to the domestic fly.

The test insects are domestic flies of mixed sexes. One operates by topical application of 1\mu l of acetonic solution to the dorsal thorax of the insects. One uses 50 individuals per treatment. One carries out the mortality check twenty-four hours after treatment and determines the lethal dose 50 of the compound.

The experimental results obtained are summarized in the following table:

<table>
<thead>
<tr>
<th>Doses</th>
<th>% mortality at 24 hrs.</th>
<th>LD&lt;sub&gt;50&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>93.3</td>
<td></td>
</tr>
<tr>
<td>3.75</td>
<td>83.2</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>68.0</td>
<td>1.6 nanogram per insect</td>
</tr>
<tr>
<td>1.25</td>
<td>34.5</td>
<td></td>
</tr>
<tr>
<td>0.625</td>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>
Conclusion: Compound A is endowed with very high insecticidal activity with respect to the domestic fly.

B - Study of the insecticidal activity with respect to larvae of Spodoptera Littoralis.

The tests are carried out by topical application. One deposits 1 µl of an acetonic solution of product to be tested on the dorsal thorax of each individual. One uses 15 Spodoptera Littoralis caterpillars in the fourth larval stage for each dose employed. After treatment the individuals are placed on an artificial nutrient medium (Poitot medium). One carries out the efficiency check (percentage mortality, taking an untreated control into account), twenty-four hours, then forty-eight hours after treatment and one determines the lethal dose 50 (LD₅₀) in nanograms per caterpillar.

The experimental results are summarized in the following table:

<table>
<thead>
<tr>
<th>Doses</th>
<th>% mortality 24 hrs.</th>
<th>% mortality 48 hrs.</th>
<th>LD₅₀ at 48 hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>95.6</td>
<td>97.8</td>
<td></td>
</tr>
<tr>
<td>0.625</td>
<td>80.0</td>
<td>82.2</td>
<td></td>
</tr>
<tr>
<td>0.3125</td>
<td>48.9</td>
<td>62.2</td>
<td>0.3 nanogram per caterpillar</td>
</tr>
<tr>
<td>0.1562</td>
<td>20.5</td>
<td>27.3</td>
<td></td>
</tr>
</tbody>
</table>
The claims defining the invention are as follows:

1. Process for converting an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) or a racemic one of structure (R,S) of formula B:

![Chemical Structure](image)

or a mixture, in non-equimolecular proportions, of an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) and an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (S), a mixture denoted by "ester(R + S)" into an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (S), characterised in that the ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) or of racemic structure (R,S), or the mixture of esters called "ester(R + S)" is subjected to the action of a basic agent selected from the group constituted by ammonia, the primary amines, the secondary...
amines, the tertiary amines, the quaternary ammonium compounds, the ion exchange resins of basic nature, the liquid amines of high molecular weight and the strong bases which, themselves, are used in catalytic amount, in a solvent or a mixture of solvents in which the ester of a chiral acid (A) with an alcohol (B) of structure (S) is insoluble and the ester of a chiral acid (A) with an alcohol (B) of structure (R) is soluble, then the ester of a chiral acid (A) with an alcohol (B) of structure (S) thus rendered insoluble is isolated from the reaction medium.

2. Process for converting an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) or a racemic one of structure (R,S) of formula B:

\[
\begin{align*}
\text{(B)} \\
\text{(R) or (R,S)}
\end{align*}
\]

or a mixture, in non-equimolecular proportions, of an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) and an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (S), a mixture denoted by "ester(R + S)" into an ester of a chiral acid (A) with an optically-active alcohol (B) of structure (S),
characterised in that the ester of a chiral acid (A) with an optically-active alcohol (B) of structure (R) or of racemic structure (R,S) or the mixture of esters called "ester(R + S)" is subjected to the action of a basic agent selected from the group constituted by ammonia, the secondary amines, the tertiary amines and the strong bases which, themselves, are used in catalytic amount, in a solvent or a mixture of solvents in which the ester of a chiral acid (A) with an alcohol (B) of structure (S) is insoluble and the ester of a chiral acid (A) with an alcohol (B) of structure (R) is soluble, then the ester of a chiral acid (A) with an alcohol (B) of structure
(8) thus rendered insoluble is isolated from the reaction medium.

3. Process according to claim 2, characterized in that the chiral acid (A) is selected from the group constituted by the acids possessing one asymmetric carbon atom and the acids possessing two asymmetric carbon atoms.

4. Process according to claim 1, characterized in that the chiral acid (A) is selected from the group constituted by the acids possessing one asymmetric carbon atom and the acids possessing two asymmetric carbon atoms, the basic agent being selected from the group constituted by the primary amines, the quaternary ammonium compounds, the ion exchange resins of basic nature and the liquid amines of high molecular weight.

5. Process according to claims 2 or 3, characterized in that the chiral acid (A) is a cyclopropane carboxylic acid of which two of the carbon atoms in the ring are asymmetric carbon atoms.

6. Process according to claims 2, 3 or 5, characterized in that the chiral acid (A) is an optically-active cyclopropane carboxylic acid of cis or trans structure of formula:

```
H3C
  /\     \ CO2H
 /  \     /
H2C     H
      /\    /\ Hal
     /  \  /  
    Hal Hal
```

in which Hal represents a chlorine or bromine atom.
7. Process according to claim 1 or 4, characterized in that the chiral acid (A) is an optically-active cyclopropane carboxylic acid of cis or trans structure of formula:

```
  H3C   CO2H
  \   /  \
  H   H
  Hal  Hal
```

in which Hal represents a chlorine or bromine atom, the basic agent being selected from the group constituted by the primary amines, the quaternary ammonium compounds, the ion exchange resins of basic nature and the liquid amines of high molecular weight.

8. Process according to claims 2, 3, 5 or 6, characterized in that the chiral acid (A) is selected from the group constituted by 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylic acid or 1R, cis 2,2-dimethyl 3-(2,2-dibromovinyl) cyclopropane carboxylic acid and 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylic acid or 1R, cis 2,2-dimethyl 3-(2,2-dichlorovinyl) cyclopropane carboxylic acid.

9. Process according to claim 1, 4 or 7, characterized in that the chiral acid (A) is selected from the group constituted by 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylic acid or 1R, cis 2,2-dimethyl 3-(2,2-dibromovinyl) cyclopropane carboxylic acid and 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylic acid or 1R, cis 2,2-dimethyl 3-(2,2-dichlorovinyl) cyclopropane carboxylic acid, the basic agent being selected from the group...
constituted by the primary amines, the quaternary ammonium compounds, the ion exchange resins of basic nature and the liquid amines of high molecular weight.

10. Process according to claim 2, 3, 5, 6 or 8, characterized in that the basic agent is selected from the group constituted by ammonia, triethylamine, diethylamine, morpholine, pyrrolidine, piperidine and, used in catalytic amount, sodium hydroxide, potassium hydroxide, the alkali alcoholates, the alkali amides and the alkali hydrides.

11. Process according to claim 2, 3, 5, 6 or 8, characterized in that the basic agent is selected from the group constituted by diisopropylamine, ephedrine, triethylene-diamine, potassium terbutylate and sodium isopropylate, both these latter bases being used in catalytic amount.

12. Process according to claim 1, 4, 7 or 9, characterized in that the basic agent is selected from the group constituted by benzylamine, n-butylamine, sec-butylamine, tetrabutylammonium hydroxide, the ion exchange resins of strongly basic nature containing quaternary ammonium compounds or amines and the amines of high molecular weight insoluble in water.

13. Process according to claim 2, 3, 5, 6, 8 or 10, characterized in that the solvent or the mixture of solvents used is selected from the group constituted by acetonitrile, the alkanols and the mixtures of alkanol and petroleum ether.

14. Process according to claim 1, 4, 7, 9, 11 or 12, characterized in that the solvent or the mixture of solvents used is selected from the group constituted by acetonitrile,
the alkanols and the mixtures of alkanol and petroleum ether.

15. Process according to claim 2, characterized in that the chiral acid (A) is 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylic acid.

16. Process according to claim 15, characterized in that the basic agent is selected from the group constituted by ammonia, triethylamine, diethylamine, morpholine, pyrrolidine, piperidine, and, used in catalytic amount, sodium hydroxide, potassium hydroxide, the alkali alcoholates, the alkali amides and the alkali hydrides and in that the solvent or the mixture of solvents used is selected from the group constituted by acetonitrile, the alkanols and the mixtures of alkanol and petroleum ether.

17. Process according to claim 15, characterized in that the basic agent is selected from the group constituted by diisopropylamine, ephedrine, triethylene diamine, potassium tertbutoxide and sodium isopropylate, both these latter bases being used in catalytic amount and in that the solvent or the mixture of solvents used is selected from the group constituted by acetonitrile, the alkanols and the mixtures of alkanol and petroleum ether.

18. Process according to claim 1, characterized in that the chiral acid (A) is 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylic acid.

19. Process according to claim 18, characterized in that the basic agent is selected from the group constituted by benzylamine, n-butylamine, sec-butylamine, tetrabutyl
ammonium hydroxide, the ion exchange resins of strongly basic nature containing quaternary ammonium compounds or amines and the amines of high molecular weight insoluble in water.

20. Process according to claim 2, characterized in that the chiral acid ester (A) of alcohol (B) is (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate.

21. Process according to claim 1, characterized in that the chiral acid ester (A) of alcohol (B) is (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dibromovinyl) cyclopropane-1R-carboxylate, the basic agent being selected from the group constituted by the primary amines, the quaternary ammonium compounds, the ion exchange resins of basic nature and the liquid amines of high molecular weight.

22. Process according to any one of claims 15 and 20, characterized in that the 2,2-dichlorovinyl derivative is used in place of the 2,2-dibromovinyl derivative.

23. Process according to any one of claims 18 and 21, characterized in that the 2,2-dichlorovinyl derivative is used in place of the 2,2-dibromovinyl derivative.

24. (S) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate.

25. (R) α-cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R-carboxylate.

26. Insecticidal compositions containing, as active principle, the product according to claim 24.

27. Insecticidal compositions containing, as active principle, the product according to claim 25.
28. A process, compound or insecticidal composition substantially as hereinbefore described or disclosed with or without reference to the Examples.

DATED this 26th day of April, 1977.

ROUSSEL-UCLAF
By its Patent Attorneys:
GALLINAN AND ASSOCIATES.

[Signature]