

PATENT SPECIFICATION

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(54) CHIRAL ACID ESTERS

(71) We, ROUSSEL UCLAF, a French Body Corporate of 35 Boulevard des Invalides, Paris 7^{ème}, France, 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:-

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).

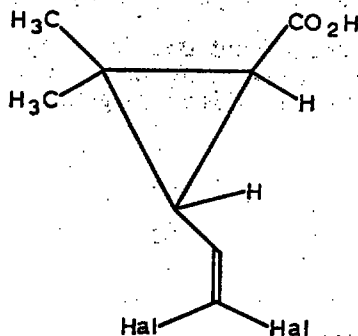
According to the present invention there is provided a process for the preparation of the ester of a chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol which comprises reacting the ester of the chiral acid and (R)- α -cyano-3-phenoxybenzyl alcohol, or a mixture thereof with the ester of the chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol, with a basic agent selected from ammonia, a primary, secondary or tertiary amine, a quaternary ammonium compound, a basic ion exchange resin, a high molecular weight liquid amine and a catalytic amount of a strong base, in the presence of a solvent in which the ester of the chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol is insoluble and the ester of the chiral acid and (R)- α -cyano-3-phenoxybenzyl alcohol is soluble and isolating the precipitated ester of the chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol from the reaction mixture.

According to one particular embodiment of the invention the basic agent is selected from ammonia, a secondary amine, a tertiary amine and a catalytic amount of a strong base.

The starting material used in the process of the invention may be the ester of the chiral acid and (R)- α -cyano-3-phenoxybenzyl alcohol or a mixture thereof i.e. a racemate or non-equimolar mixture with the ester of the chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol.

The chiral acid can be an acid having one or more asymmetric carbon atoms, for example two asymmetric carbon atoms such as a cyclopropane carboxylic acid in which two of the carbon atoms in the ring are asymmetric.

Preferred chiral cyclopropane carboxylic acids are the optically-active cyclopropane carboxylic acids of cis or trans structure of formula:



in which Hal represents a chlorine or bromine atom.

According to a simplified nomenclature recently adopted, such acids having the (1R,3R) structure are denoted hereinafter as being (1R, cis) acids.

Particularly preferred chiral cyclopropane carboxylic acids for use in the process of the

invention are the following:

2,2-dimethyl-3R-(2,2-dibromovinyl)-cyclopropane-1R-carboxylic acid (1R, *cis* 2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropane-carboxylic acid) and 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylic acid (1R, *cis* 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane-carboxylic acid).

The basic agent used in the process of the invention is preferably ammonia, triethylamine, diethylamine, morpholine, pyrrolidine, piperidine or a catalytic amount of sodium hydroxide, potassium hydroxide or an alkali alcoholate, amide or hydride, most preferred being ammonia or triethylamine. Alternative bases which may, however, be used if desired include, for example, diisopropylamine, ephedrine, triethylenediamine, benzylamine, n-butylamine, sec.butylamine, tetrabutylammonium hydroxide and a catalytic amount of potassium *tert*butylate or sodium isopropylate.

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" [registered Trade Mark] and the company ROHM and HAAS sells similar basic agents under the name "AMBERLITE" [registered Trade Mark].

These commercial products are advantageously used as basic agents in the process of the invention.

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

The basic agents 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 of the invention, for example LIQUID "AMBERLITES" of type LA1 or LA2.

The solvent used in the process of the invention preferably comprises acetonitrile, an alkanol or a mixture of an alkanol and petroleum ether, especially a mixture of an alkanol and pentane, hexane or heptane. A particularly preferred solvent comprises acetonitrile, propanol, isopropanol, a straight chain or branched butanol or mixtures thereof with "essence G" (petroleum ether, b.pt. 35-70°C), "essence B" (petroleum ether, b.pt. 65-70°C), "essence C" (petroleum ether, b.pt. 70-97°C), "essence E", (petroleum ether, b.pt. 86-122°C) pentane, hexane or heptane.

Isopropanol is particularly interesting for use in carrying out the process of the invention.

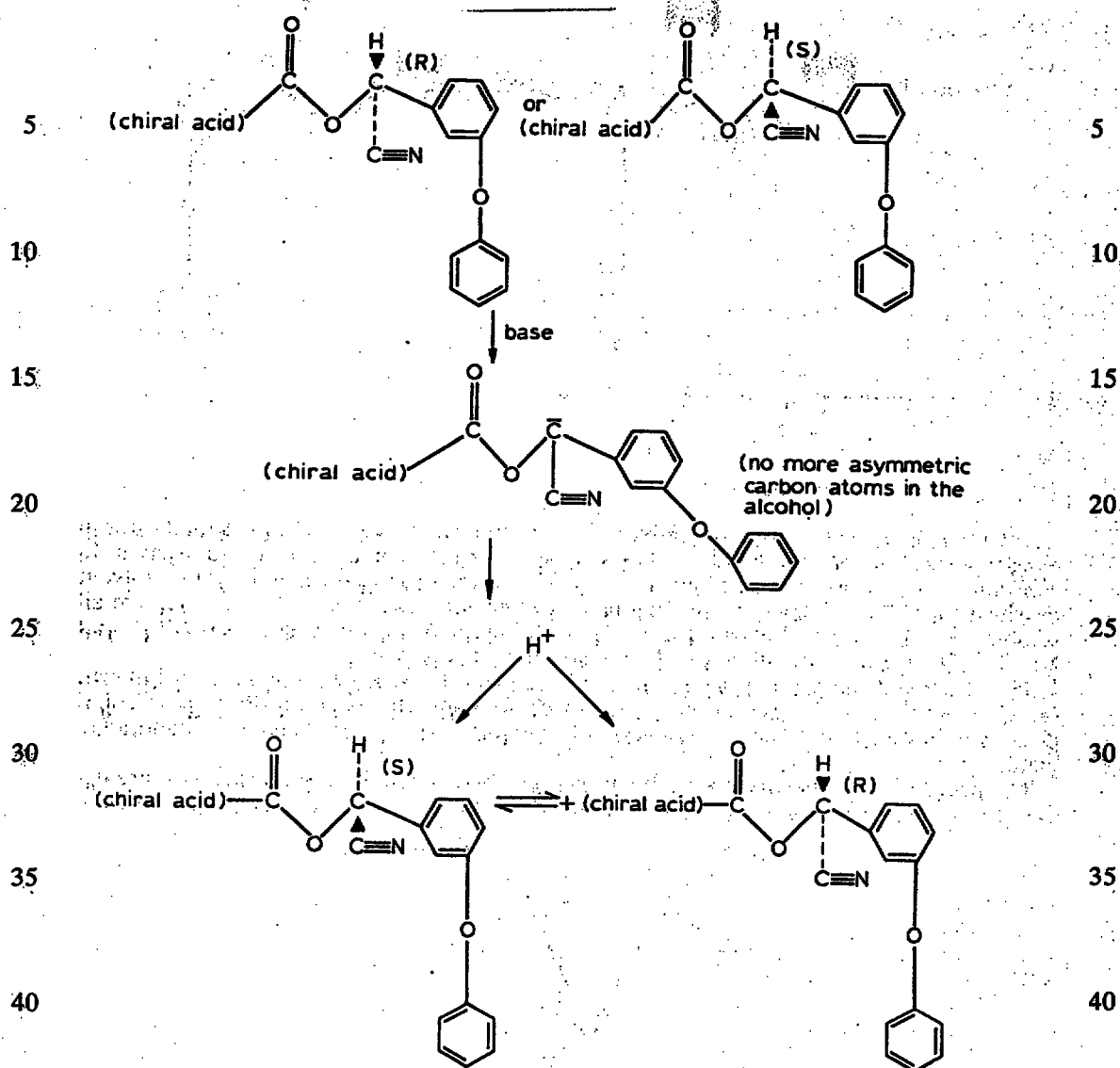
It will be appreciated that, in the solvents used according to the process of the invention, the (S) alcohol esters may show a slight solubility. Provided, however, that the solubility is sufficiently slight and taking into account the volume of solvent used, good yields may still be obtained. In general, depending on the solvent used as well as the volume of solvent, a yield by weight of (S) alcohol ester of at least 80% may be obtained.

The (R) alcohol esters used as starting materials in the process of the invention are generally very soluble in the solvents used such that a small volume of solvent enables them to be dissolved totally.

The temperature of the reaction is not critical and merely influences the speed of the reaction, as does the precise nature of the base.

Whilst we do not wish to be limited by theoretical considerations it is believed that, by the action of the base the ester of the chiral acid and alcohol of structure (R) contained in the starting material gives rise to an α -cyano carbanion causing racemisation of the corresponding carbon atom.

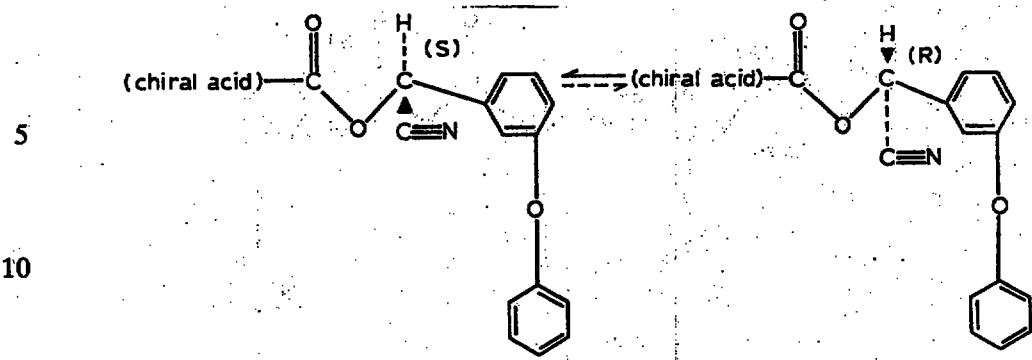
Subsequent protonation in the solvent then leads, for the soluble fraction, to the formation, in equimolecular proportions of the two diastereoisomers [(S) alcohol ester and (R) alcohol ester] according to the following diagram :



45 In the solvent used according to the process of the invention, the ester of the chiral acid and the alcohol of structure (S) being insoluble and the ester of the chiral acid and the alcohol of structure (R) being soluble, the equilibrium is then displaced towards the formation of the (S) alcohol ester resulting, in practice, in yields of the desired (S) alcohol ester of 80 to 90% with reference to the optically-active starting ester employed.

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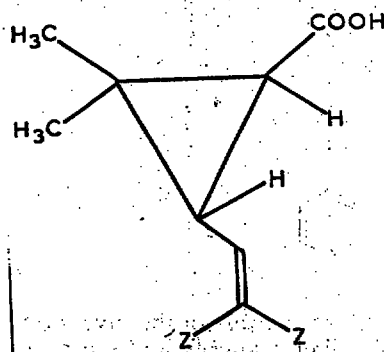
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The intermediate formation of a mixture of the (S) alcohol ester and (R) alcohol ester in equimolar proportions can be illustrated by evaporating the soluble fraction to dryness. In contradistinction to the present invention when the same process is carried out in a solvent in which the (S) alcohol ester, the (R) alcohol ester and the racemic alcohol ester are all soluble, as described and claimed in our British Patent Application No. 16864/77 (Serial No. 1582594), substantially complete racemisation takes place.

The process of the present invention is of a particularly unexpected nature, for hitherto there did not exist, as far as is known, any process for converting an optically-active alcohol ester into an optically-active alcohol ester of antipodal structure in 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 :



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

For several years insecticidal compounds endowed with exceptionally high activity have been prepared by esterifying the chiral acids mentioned above with α -cyano-3-phenoxybenzyl alcohol.

Moreover it has been in general proved that the esters of the chiral acids mentioned above and (S) α -cyano-3-phenoxybenzyl alcohol possess an insecticidal activity which is much higher than that of the corresponding esters of the racemic (R,S) or (R) alcohol.

Now α -cyano-3-phenoxybenzyl alcohol is generally obtained by synthetic routes in the form of a racemic compound. The weakness of its molecule, moreover, does not permit stereo selective preparation of the enantiomers, nor resolution of the racemic alcohol to be considered.

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

The (R) alcohol ester or the mixture of (R) alcohol ester and (S) alcohol ester rich in the (R) alcohol ester resulting from such a separation was also not easily recoverable from the preparation of the (S) alcohol esters.

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

The process of the invention using only one stage and employing simple working procedures and readily available 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 (S) α -cyano-3-phenoxybenzyl alcohol, 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, which have not previously been described in the literature, are described and claimed in our co-pending Application No. 16867/77 (Serial No. 1582596) as well as insecticidal compositions containing them.

The first of these compounds, that is to say the (S) alcohol ester 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, mosquitos).

Tests given in the experimental portion illustrate the 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 strong than that of the corresponding (S) alcohol ester.

As indicated above (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 may be incorporated as an active principle in insecticidal compositions.

In these 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, an alcohol, a hydrocarbon or some other organic solvent, a mineral, animal or vegetable oil, a powder such as talc, a clay, a silicate 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-trioxadodecyl-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-butoxyethoxy)-ethyl acetal (or tropital).

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

The following non-limiting Examples illustrate the invention.

Example 1: 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.

Into 2.5 cm³ of isopropanol one introduces 1 g of (R) α -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 cm³ of an aqueous solution of 22° Bé ammonia, agitates for eighteen hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it, dries it and obtains 0.9 g of (S) α -cyano-3-phenoxybenzyl-2,2-dimethyl-3R-(2,2-dibromovinyl)-cyclopropane-1R-carboxylate, M.Pt. = 100°C, $[\alpha]_D^{20} = +60.5^\circ$ (c = 1%, benzene), $[\alpha]_D^{20} = +25^\circ$ (c = 1%, chloroform).

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

		C%	H%	N%	Br%	
5	Calculated	52.3	3.79	2.77	31.63	5
	Found	52.2	4.0	2.7	31.5	

10 *Example 2: 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.* 10

Starting with 1 g of the (R) alcohol ester, operating in a manner similar to that of Example 1 but using 0.30 cm³ of an aqueous solution of 22° Bé ammonia, one obtains 0.9 g of (S) alcohol ester of the same quality as in Example 1.

15 *Example 3: 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.* 15

20 Starting with 1 g of (R) alcohol ester, 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 (S) alcohol ester of the same quality as in Example 1. 20

25 *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.* 25

Starting with 1 g of (R) alcohol ester, 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 (S) alcohol ester of the same quality as in Example 1.

30 *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.* 30

35 Starting with 1 g of (R) alcohol ester, 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 (S) alcohol ester of the same quality as in Example 1. 35

40 *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.* 40

Starting with 1 g of (R) alcohol ester, 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 (S) alcohol ester of the same quality as in Example 1.

45 *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.* 45

Starting with 1 g of (R) alcohol ester, 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 (S) alcohol ester of the same quality as in Example 1.

50 *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.* 50

55 Starting with 1 g of (R) alcohol ester, 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 (S) alcohol ester of the same quality as in Example 1. 55

60 *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.* 60

Starting with 1 g of (R) alcohol ester, operating in a manner similar to that of Example 1 but replacing the 2.5 cm³ of isopropanol with 2.5 cm³ of tertbutanol, one obtains 0.85 g of (S) alcohol ester 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 cm³ of acetonitrile and 0.5 cm³ of water one dissolves 1 g of (R) alcohol ester, adds 0.15 cm³ of an 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 (S) alcohol ester 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 (R) alcohol ester, using the same *modus operandi* as in Example 9, using 2.5 cm³ of terbutanol but replacing the ammonia with 0.16 g of triethylamine, one obtains 0.8 g of (S) alcohol ester 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 (R) alcohol ester, using the same *modus operandi* as in Example 8 using 2.5 cm³ of butanol but replacing the ammonia with 0.11 g of pyrrolidine, one obtains 0.8 g of (S) alcohol ester 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, $[\alpha]_D^{20} = 0^\circ$ to -1° ($c = 1\%$, chloroform) and $[\alpha]_D^{20} = +14^\circ$ ($c = 1\%$, benzene), are dissolved in 262.5 cm³ of isopropanol. To the solution one adds 15 cm³ of an aqueous solution of 22° Bé ammonia, agitates for eighteen hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with 105 cm³ 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.Pt. = 100°C, $[\alpha]_D^{20} = +60.5^\circ$ ($c = 1\%$, 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 cm³ of isopropanol one introduces 1 g of racemic (R,S) alcohol ester, adds 0.30 cm³ of an aqueous solution of 22° Bé ammonia, agitates for twenty hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with 1 cm³ of isopropanol, dries it and obtains 0.9 g of (S) alcohol ester of the same quality as in Example 1.

Example 15: 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 cm³ of isopropanol one introduces 1 g of racemic (R,S) alcohol ester, adds 0.16 g of triethylamine, agitates for fifteen hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with 1 cm³ of isopropanol, dries it and obtains 0.87 g of (S) alcohol ester of the same quality as in Example 1.

Example 16: 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 cm³ of isopropanol one introduces 1 g of racemic (R,S) alcohol ester, adds 0.32 g of triethylamine, agitates for fifteen hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with 1 cm³ of isopropanol, dries it and obtains 0.9 g of (S) alcohol ester of the same quality as in Example 1.

Example 17: 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 cm³ of isopropanol one introduces 1 g of racemic (R,S) alcohol ester, adds 0.13 g of morpholine, agitates for ninety-six hours at 20°C, isolates by vacuum-filtration the precipitate formed, washes it with 1 cm³ of isopropanol, dries it and obtains 0.9 g of (S)

alcohol ester of the same quality as in Example 1.

Example 18: 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 cm³ 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 cm³ of isopropanol, dries it and obtains 0.85 g of (S) alcohol ester of the same quality as in Example 1.

Example 19: 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 1 g of racemic (R,S) alcohol ester in a mixture of 2 cm³ of acetonitrile and 0.5 cm³ of water, adds 0.15 cm³ of an aqueous solution of 22° Bé ammonia, agitates for seventeen 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 (S) alcohol ester 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 (R) alcohol ester.

a) Preparation of a mixture of (R) alcohol and (S) alcohol esters:

One introduces 10 g of (R,S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dibromovinyl)-cyclopropane-1R-carboxylate, $[\alpha]_D^{20} = 0^\circ$, -1° ($c = 1\%$, chloroform) and $[\alpha]_D^{20} = +14^\circ$ ($c = 1\%$, 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 (S) alcohol ester. M.Pt. = 100°C, $[\alpha]_D^{20} = +60^\circ$ ($c = 1\%$, 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 (R) alcohol ester and (S) alcohol ester into (S) alcohol ester:

To the solution L one adds 0.8 cm³ of an 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-dibromovinyl)-cyclopropane-1R-carboxylate. M.Pt. = 100°C, $[\alpha]_D^{20} = +60^\circ$ ($C = 1\%$, 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 (R) alcohol ester:

10 g of racemic (R,S) alcohol ester, of $[\alpha]_D^{20} = +16.5^\circ$ ($c = 10\%$, 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) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate of $[\alpha]_D^{20} = 31^\circ$ ($c = 1\%$, benzene) or $[\alpha]_D^{20} = -21.5^\circ$ ($c = 1\%$, chloroform).

b) Conversion into (S) alcohol ester:

To 60 g of (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate $[\alpha]_D^{20} = -31^\circ$ ($c = 1\%$, benzene) or $[\alpha]_D^{20} = -21.5^\circ$ ($c = 1\%$, chloroform) obtained in paragraph a) one adds 120 cm³ of isopropanol then 9 cm³ of an 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 cm³ of isopropanol at -20°C, dries it and obtains 48.5 g of (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate. M.Pt. = 60°C, $[\alpha]_D^{20} = +66^\circ$ ($c = 1\%$, benzene) or $[\alpha]_D^{20} = +34^\circ$ ($c = 1\%$, chloroform).

Example 22: Conversion of (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.

To 600 g of racemic (R,S) alcohol ester, $[\alpha]_D^{20} = +16.5^\circ$ ($c = 10\%$, benzene) one adds 1200 cm³ of isopropanol, then introduces into the solution obtained 90 cm³ of an 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 cm³ of isopropanol at -20°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°C, $[\alpha]_D^{20} = +66^\circ$ ($c = 1\%$, benzene) or $[\alpha]_D^{20} = +34^\circ$ ($c = 1\%$, chloroform).

Analysis:

C₂₂H₁₉O₃NCl₂ (416.28)

	C%	H%	N%	Cl%
Calculated	63.48	4.60	3.36	17.03
Found	63.7	4.6	3.4	17.1

Example 23: Conversion of (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'-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° ($c = 1\%$, chloroform) and $[\alpha]_D^{20} = +14^\circ$ ($c = 1\%$, benzene) in 25 cm³ of isopropanol, adds 0.8 g of diisopropylamine, agitates for six hours at 20°C then two hours at 0°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 48 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 $[\alpha]_D^{20} = +56.5^\circ$ ($c = 4\%$, 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, $[\alpha]_D^{20} = 0^\circ$ to -1° ($c = 1\%$, chloroform) and $[\alpha]_D^{20} = +14^\circ$ ($c = 1\%$, 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-1R-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 (RS) alcohol ester, 8.85 g of (S) alcohol ester 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 (RS) alcohol ester, 8.7 g of (S) alcohol ester 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 triethylene diamine (or "Dabco" [registered Trade Mark]) and one obtains, after seventy-two hours' agitation at 20°C, 7.5 g of (S) alcohol ester 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 (R,S) alcohol ester in 25 cm³ of isopropanol, adds 0.23 g of potassium *tert*-butoxide, agitates for eighteen hours at 20°C and obtains 7.7 g of (S) alcohol ester 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 *tert*-butoxide with 0.34 g of sodium isopropoxide, agitating for twenty-four hours at 20°C, and one obtains 7.3 g of (S) alcohol ester 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, $[\alpha]_D^{20} = 0^\circ$ to 1° (*c* = 1%, chloroform) and $[\alpha]_D^{20} = +14^\circ$ (*c* = 1%, benzene), in 25 cm³ 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, $[\alpha]_D^{20} = +57^\circ$ (*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 (R,S) alcohol ester 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, washes it and dries it and obtains 9.0 g of (S) alcohol ester 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 (S) alcohol ester of the same quality as in Examples 23 to 33.

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 *tert*-butoxide with 0.64 cm³ of 40% aqueous solution of *tetrabutyl ammonium hydroxide*, one obtains, after twenty-four hours' agitation at 20°C, 8.4 g of (S) alcohol ester 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 (R,S) alcohol ester in 25 cm³ of isopropanol, 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 N sodium hydroxide, then with water, one agitates for twenty-four hours at 20°C, isolates by vacuum-filtration the precipitate (mixture of resin and (S) alcohol ester), adds methylene

chloride thereto, agitates, filters, concentrates the filtrate to dryness and obtains 7.8 g of (S) alcohol ester of the same quality as in Examples 23 to 35.

5 *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.* 5

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 slightly 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 (S) alcohol ester of identical quality to the products obtained in Examples 23 to 36. 10

15 *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.* 15

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 (S) alcohol ester of quality identical to that of the products obtained in Examples 23 to 37. 20

25 *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.* 25

One operates in a manner similar to that of Example 36 but using 10 g of liquid "AMBERLITE" LA1 (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 (S) alcohol ester of the same quality as the products obtained in Examples 23 to 38.

30 *Example 40: 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.* 30

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 (S) alcohol ester of identical quality to that of the products obtained in Examples 23 to 39. 35

40 *Example 41: 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.* 40

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 (S) alcohol ester of the same quality as that obtained in Examples 23 to 40.

45 *Example 42: Composition based upon (S) α-cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate.* 45

One mixes:

50	(S) α-cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate	25 g/l	50
	-2,6-di-tert-butyl paracresol	10 g/l	
	-"EMCOL" [registered Trade Mark] H 300 B *	50 g/l	
	-EMCO H 500 B *	20 g/l	
	-"Supersol" [registered Trade Mark]	786 g/l	

55 * 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. 55

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

60 *Study of the insecticidal activity of (S) α-cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate (Compound A).* 60

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 µl of an acetonic solution to the dorsal thorax of the insects. One uses 50 individuals per treatment. One carries out a mortality check twenty-four hours after treatment and 65

determines the lethal dose (LD_{50}) of the compound.

The experimental results obtained are summarized in the following table:

	Dose	% mortality at 24 hrs.	LD_{50}	
5	5.	93.3		5
	3.75	83.2		
	2.5	68.0	1.6 nanogram per insect	
10	1.25	34.5		10
	0.625	10.0		

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 μ l of an acetonetic 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 carried 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 (LD_{50}) in nanograms per caterpillar.

The experimental results are summarized in the following table:

	Dose	% mortality		LD_{50} at	
		24 hrs.	48 hrs.	48 hrs.	
30	1.25	95.6	97.8		30
	0.625	80.0	82.2	0.3 nanogram per caterpillar	
	0.3125	48.9	62.2		
	0.1562	20.5	27.3		

WHAT WE CLAIM IS:-

1. A process for the preparation of the ester of a chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol which comprises reacting the ester of the chiral acid and (R)- α -cyano-3-phenoxybenzyl alcohol, or a mixture thereof with the ester of the chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol, with a basic agent selected from ammonia, a primary, secondary or tertiary amine, a quaternary ammonium compound, a basic ion exchange resin, a high molecular weight liquid amine and a catalytic amount of a strong base, in the presence of a solvent in which the ester of the chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol is insoluble and the ester of the chiral acid and (R)- α -cyano-3-phenoxybenzyl alcohol is soluble and isolating the precipitated ester of the chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol from the reaction mixture.

2. A process as claimed in claim 1 wherein the basic agent is ammonia, triethylamine, diethylamine, diisopropylamine, ephedrine, triethylenediamine, benzylamine, n-butylamine, sec-butylamine, morpholine, pyrrolidine, piperidine, tetrabutylammonium hydroxide or a catalytic amount of sodium hydroxide, potassium hydroxide or an alkali metal alcoholate, amide or hydride.

3. A process as claimed in claim 2 wherein the basic agent is a catalytic amount of potassium *tert*-butoxide or sodium isopropoxide.

4. A process as claimed in any of the preceding claims wherein the solvent comprises acetonitrile, an alkanol or a mixture of an alkanol and petroleum ether.

5. A process as claimed in claim 4 wherein the solvent comprises propanol, isopropanol, a straight chain or branched butanol or mixtures thereof with "essence G", "essence B", "essence C", "essence E", pentane, hexane or heptane.

6. A process as claimed in any of the preceding claims wherein the chiral acid has at least one asymmetric carbon atom.

7. A process as claimed in claim 6 wherein the chiral acid has two asymmetric carbon atoms.

8. A process as claimed in claim 7 wherein the chiral acid is a cyclopropane carboxylic acid in which two of the ring carbon atoms are asymmetric.

9. A process as claimed in claim 8 wherein the chiral acid is an acid of formula I,

(17)



determines the lethal dose (LD₅₀) of the compound.
The experimental results obtained are summarized in the following table:

5	Dose	% mortality at 24 hrs.	LD ₅₀	5
	5.	93.3		
	3.75	83.2		
	2.5	68.0		
10			1.6 nanogram per insect	10
	1.25	34.5		
	0.625	10.0		

15 **Conclusion:** Compound A is endowed with very high insecticidal activity with respect to the domestic fly. 15

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

20 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 carried 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 (LD₅₀) in nanograms per caterpillar. 20

25 The experimental results are summarized in the following table: 25

	Dose	% mortality 24 hrs.	% mortality 48 hrs.	LD ₅₀ at 48 hrs.	
30	1.25	95.6	97.8		30
	0.625	80.0	82.2		
	0.3125	48.9	62.2	0.3 nanogram per caterpillar	
	0.1562	20.5	27.3		

35 **WHAT WE CLAIM IS:-** 35

1. A process for the preparation of the ester of a chiral acid and (S)-α-cyano-3-phenoxybenzyl alcohol which comprises reacting the ester of the chiral acid and (R)-α-cyano-3-phenoxybenzyl alcohol, or a mixture thereof with the ester of the chiral acid and (S)-α-cyano-3-phenoxybenzyl alcohol, with a basic agent selected from ammonia, a primary, secondary or tertiary amine, a quaternary ammonium compound, a basic ion exchange resin, a high molecular weight liquid amine and a catalytic amount of a strong base, in the presence of a solvent in which the ester of the chiral acid and (S)-α-cyano-3-phenoxybenzyl alcohol is insoluble and the ester of the chiral acid and (R)-α-cyano-3-phenoxybenzyl alcohol is soluble and isolating the precipitated ester of the chiral acid and (S)-α-cyano-3-phenoxybenzyl alcohol from the reaction mixture. 40
2. A process as claimed in claim 1 wherein the basic agent is ammonia, triethylamine, diethylamine, diisopropylamine, ephedrine, triethylenediamine, benzylamine, n-butylamine, sec.-butylamine, morpholine, pyrrolidine, piperidine, tetrabutylammonium hydroxide or a catalytic amount of sodium hydroxide, potassium hydroxide or an alkali metal alcoholate, amide or hydride. 50
3. A process as claimed in claim 2 wherein the basic agent is a catalytic amount of potassium *tert*butylate or sodium isopropylate.
4. A process as claimed in any of the preceding claims wherein the solvent comprises acetonitrile, an alkanol or a mixture of an alkanol and petroleum ether. 55
5. A process as claimed in claim 4 wherein the solvent comprises propanol, isopropanol, a straight chain or branched butanol or mixtures thereof with "essence G", "essence B", "essence C", "essence E", pentane, hexane or heptane.
6. A process as claimed in any of the preceding claims wherein the chiral acid has at least one asymmetric carbon atom. 60
7. A process as claimed in claim 6 wherein the chiral acid has two asymmetric carbon atoms.
8. A process as claimed in claim 7 wherein the chiral acid is a cyclopropane carboxylic acid in which two of the ring carbon atoms are asymmetric.
- 65 9. A process as claimed in claim 8 wherein the chiral acid is an acid of formula I, 65



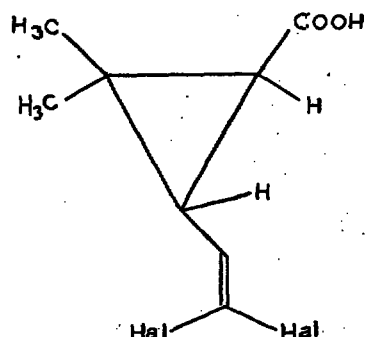
* C L H S *

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(wherein Hal represents a chlorine or bromine atom).

10. A process as claimed in claim 9 wherein the chiral acid is 2,2-dimethyl-3R-(2,2-dibromovinyl)-cyclopropane-1R-carboxylic acid.

11. A process as claimed in claim 9 wherein the chiral acid is 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylic acid.

12. A process as claimed in claim 10 or claim 11 wherein the basic agent is ammonia or triethylamine.

13. A process as claimed in any of claims 10 to 12 wherein the solvent is isopropanol.

14. A process as claimed in any of the preceding claims wherein the (R)- α -cyano-3-phenoxybenzyl chiral acid ester is reacted with the basic agent.

15. A process as claimed in any of claims 1 to 13 wherein the (R,S)- α -cyano-3-phenoxybenzyl chiral acid ester is reacted with the basic agent.

16. A process as claimed in any of claims 1 to 13 wherein a non-equimolar mixture of the (R)- α -cyano-3-phenoxybenzyl and (S)- α -cyano-3-phenoxybenzyl chiral acid ester is reacted with the basic agent.

17. A process as claimed in claim 1 wherein the basic agent is selected from ammonia, secondary or tertiary amines and a catalytic amount of a strong base.

18. A process for the preparation of the ester of a chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol as defined in claim 1 substantially as herein described.

19. A process for the preparation of the ester of a chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol substantially as herein described in Examples 1 to 41.

20. A process for the preparation of the ester of a chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol substantially as herein described in Examples 1 to 22.

21. Esters of a chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol whenever prepared by a process as claimed in any of claims 1 to 16, 18 and 19.

22. Esters of a chiral acid and (S)- α -cyano-3-phenoxybenzyl alcohol whenever prepared by a process as claimed in claim 17 or claim 20.

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