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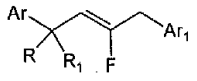
Process and Intermediate Compounds for the Preparation of Pesticidal Fluoroolefin Compounds

Abstract

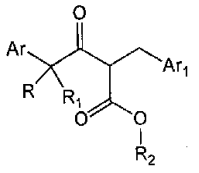
The present invention provides a process for the preparation of pesticidal fluoroolefin compounds having the structural formula I



I

wherein R is hydrogen or alkyl, and R_1 is alkyl, haloalkyl or cyclopropyl, or R and R_1 are taken together wit h the carbon atom to which they are attached to form a cyclopropyl group; Ar is phenyl optionally substituted with up to three groups, or 1- or 2-naphthyl optionally substituted with up to three groups; Ar_1 is phenoxyphenyl optionally substituted with up to five groups, biphenyl optionally substituted with up to five groups, benzylphenyl optionally substituted with up to five groups, or benzoylphenyl optionally substituted with up to five groups; and the configuration of the groups $ArCRR_1$- and -CH_2Ar_1 about the double bond is predominantly mutually trans, which process comprises

a) fluorinating a 4-aryl-3-oxo-2-(substituted benzyl)butanoate compound having the structural formula II

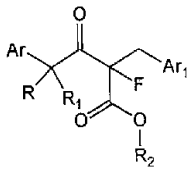


II

wherein R_2 is alkyl and Ar, Ar_1, R and R_1 are as described above in the presence of a first base to form a 4-aryl-2-fluoro-3-oxo-2-(substituted benzyl)butanoate compound having the structural formula III

wherein Ar, Ar_1, R, R_1 and R_2 are as described above,

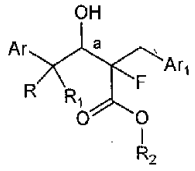
b) reducing the formula III compound to form a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoate compound having the structural formula IV



III

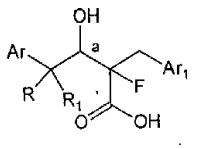
wherein Ar, Ar_1, R, R_1 and R_2 are as described above and the configuration of the groups $ArCRR_1CH(OH)$- and -$CF(CO_2R_2)CH_2Ar_1$ attached to the bond labelled "a" is predominantly R,S or S,R or a mixture thereof;

c) saponifying the formula IV compound to form a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoic acid compound having the structural formula V



IV

wherein Ar, Ar_1, R and R_1 are as described above and the configuration of the groups $ArCRR_1CH(OH)$- and -$CF(CO_2H)CH_2Ar_1$ attached to d the bond labelled "a" is predominantly R,S or S,R or a mixture thereof;



V

and d) reacting the formula V compound with a sulfonyl halide compound and a second base.

The present invention also provides intermediate compounds which are utilized in the process of this invention.

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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

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Invention Title: Process and Intermediate Compounds for the Preparation of Pesticidal Fluoroolefin Compounds

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

PROCESS AND INTERMEDIATE COMPOUNDS FOR THE PREPARATION OF PESTICIDAL FLUOROOLEFIN COMPOUNDS

BACKGROUND OF THE INVENTION

Fluoroolefin compounds which are useful as pesticidal agents are described in WO 94/06741 and GB 2,288,803-A. Those patent applications also describe processes for the preparation of fluoroolefin compounds. However, those processes are not entirely satisfactory because they require the use of Grignard reagents, alkali metal compounds and transition metal catalysts. In addition, those processes produce the fluoroolefin compounds in relatively low yields.

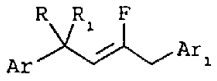
It is, therefore, an object of the present invention to provide a novel, effective and efficient process for the preparation of pesticidal fluoroolefin compounds which does not require the use of Grignard reagents, alkali metal compounds and transition metal catalysts.

It is also an object of the present invention to provide intermediate compounds which are useful for the preparation of pesticidal fluoroolefin compounds.

Other objects and advantages of the present invention will be apparent to those skilled in the art from the description below and the appended claims.

SUMMARY OF THE INVENTION

The present comprises a process for the preparation of a pesticidal fluoroolefin compound having the structural formula I



(I)

wherein

R is hydrogen or C_1-C_4alkyl, and

R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl or cyclopropyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or 1- or 2-naphthyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

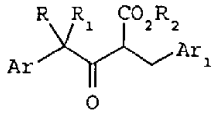
Ar_1 is phenoxyphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, biphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, benzylphenyl optionally substituted with up to five groups independently selected from halogen

atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or benzoylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups; and

the configuration of the groups $ArCRR_1$- and $-CH_2Ar_1$ about the double bond is predominantly mutually trans,

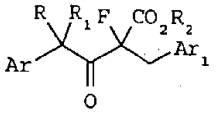
which process comprises

a) fluorinating a 4-aryl-3-oxo-2-(substituted benzyl)butanoate compound having the structural formula II



(II)

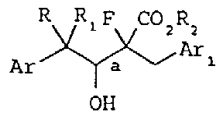
wherein R_2 is C_1-C_6alkyl and Ar, Ar_1, R and R_1 are as described above in the presence of a first base to form a 4-aryl-2-fluoro-3-oxo-2-(substituted benzyl)butanoate compound having the structural formula III



(III)

wherein Ar, Ar_1, R, R_1 and R_2 are as described above;

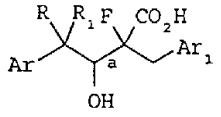
b) reducing the formula III compound to form a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoate compound having the structural formula IV



(IV)

wherein Ar, Ar_1, R, R_1 and R_2 are as described above and the configuration of the groups $ArCRR_1CH(OH)$- and $-CF(CO_2R_2)CH_2Ar_1$ attached to the bond labelled "a" is predominantly R,S or S,R or a mixture thereof;

c) saponifying the formula IV compound to form a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoic acid compound having the structural formula V



(V)

wherein Ar, Ar_1, R and R_1 are as described above and the configuration of the groups $ArCRR_1CH(OH)$- and $-CF(CO_2H)CH_2Ar_1$ attached to the bond labelled "a" is predominantly R,S or S,R or a mixture thereof; and

d) reacting the formula V compound with a sulfonyl halide compound and a second base.

The present invention further comprises the intermediate compounds of formulas III, IV and V.

DETAILED DESCRIPTION OF THE INVENTION

A preferred embodiment of the present invention comprises

a) fluorinating the formula II compound with at least about one molar equivalent of a fluorinating agent

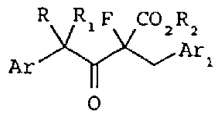
in the presence of at least about one molar equivalent of a first base, preferably in a temperature range of about -15 °C to 100 °C, in the presence of a first solvent to form a 4-aryl-2-fluoro-3-oxo-2-(substituted benzyl)-butanoate of formula III;

b) reducing the formula III compound with at least about one molar equivalent of a reducing agent, preferably in a temperature range of about -50 °C to 80 °C, in the presence of a second solvent to form a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoate of formula IV;

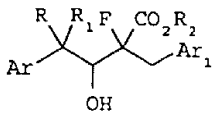
c) saponifying the formula IV compound by reaction with at least about one molar equivalent of a base, followed by at least about one molar equivalent of an acid, preferably in a temperature range of about -15 °C to 80 °C and in the presence of a third solvent, to form a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoic acid of formula V; and

d) reacting the formula V compound with at least about one molar equivalent of a sulfonyl halide compound and at least about one molar equivalent of a second base, preferably in a temperature range of about 0 °C to 130 °C, optionally in the presence of a fourth solvent.

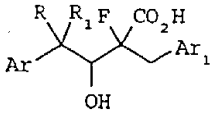
The present invention also includes the 4-aryl-2-fluoro-3-oxo-2-(substituted benzyl)butanoate compounds, the 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)-butanoate compounds, and the 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoic acid compounds which are utilized in the process of this invention. Those compounds are represented by the structural formulas III, IV and V, respectively,



(III)



(IV)



(V)

wherein

R is hydrogen or C_1-C_4alkyl, and

R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl or cyclopropyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or 1- or 2-naphthyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

Ar_1 is phenoxyphenyl optionally substituted with up to five groups independently selected from halogen

atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,

biphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,

benzylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or

benzoylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

and

R_2 is C_1-C_6alkyl; and

the optical isomers and diastereomers thereof.

Exemplary of halogen hereinabove are fluorine, chlorine, bromine and iodine. The terms "C_1-C_4haloalkyl" and "C_1-C_4haloalkoxy" are defined as a C_1-C_4alkyl group and a C_1-C_4alkoxy group substituted with one or more halogen atoms, respectively.

The product formula I compounds may be isolated by diluting the reaction mixture with water and extracting the product with a suitable extraction solvent. In the isolation procedure, conventional extraction solvents such as ether, ethyl acetate, toluene, methylene chloride and the like may be utilized.

Advantageously, the unique process of this invention provides pesticidal fluoroolefin compounds in relatively high yields. In addition, the process of this invention does not utilize the uneconomical reagents required by the prior art processes.

Fluorinating agents suitable for use in this invention include, but are not limited to, fluorine,

diethylaminosulfur trifluoride, 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), N-fluoropyridinium pyridine heptafluorodiborate, N-fluorobenzenesulfonimide, N-fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzothiazol-1,1-dioxide, an N-fluoro oxathiazinone dioxide, and the like, and mixtures thereof. N-Fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzothiazol-1,1-dioxide is a preferred fluorinating agent.

Reducing agents suitable for use in the present invention produce formula IV compounds wherein the configuration of the groups $ArCRR_1CH(OH)-$ and $-CF(CO_2R_2)CH_2Ar_1$ is predominantly R,S or S,R or a mixture thereof. Reducing agents which may be utilized in this invention include, but are not limited to, enzymatic reduction systems, whole cell microorganisms, borohydrides such as sodium borohydride, sodium cyano borohydride, zinc borohydride and the like, substituted aluminum hydrides such as lithium tri-*tert*-butoxyaluminum hydride and the like, aluminum C_1-C_6alkoxide/C_1-C_6alcohol complexes such as an aluminum isopropoxide/isopropanol complex and the like, and hydrogen in the presence of a noble metal catalyst. Borohydrides are preferred reducing agents.

Bases suitable for use in the saponification step of the present invention include, but are not limited to, alkali metal carbonates such as sodium carbonate and potassium carbonate, alkaline earth metal carbonates such as calcium carbonate, alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, alkaline earth metal hydroxides such as calcium hydroxide, alkali metal C_1-C_6alkoxides such as sodium ethoxide and potassium *tert*-butoxide, alkaline earth metal C_1-C_6alkoxides, thallium(I) carbonate, thallium(I) C_1-C_6alkoxides, and thallium(I)

hydroxide, and mixtures thereof, with alkali metal hydroxides being preferred. Acids suitable for use in this invention include mineral acids such as hydrochloric acid, hydrobromic acid, sulfuric acid and the like, and strong organic acids such as trifluoroacetic acid and the like, and mixtures thereof, with mineral acids being preferred.

Sulfonyl halide compounds suitable for use in the present invention include, but are not limited to, alkylsulfonyl chlorides such as methanesulfonyl chloride and the like, and arylsulfonyl chlorides such as *p*-toluenesulfonyl chloride, benzenesulfonyl chloride and the like, and mixtures thereof.

First bases suitable for use in the present invention include, but are not limited to, alkali metal C_1-C_6alkoxides such as sodium ethoxide and potassium *tert*-butoxide, alkali metal hydrides such as sodium hydride, alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, alkaline earth metal hydroxides such as calcium hydroxide, alkyl lithiums such as *n*-butyllithium and *s*-butyllithium, aryl lithiums such as phenyl lithium, alkaline earth metal C_1-C_6alkoxides, thallium(I) C_1-C_6alkoxides, and thallium(I) hydroxide, and mixtures thereof. Preferred first bases include alkali metal C_1-C_6alkoxides and alkali metal hydrides. Second bases suitable for use in this invention include, but are not limited to, tertiary amines such as tri(C_1-C_4alkyl)amines, pyridine and substituted pyridines, with pyridine being preferred.

First solvents suitable for use in the fluorinating step of the present invention include, but are not limited to, ethers such as tetrahydrofuran, dioxane and the like, aromatic hydrocarbons such as toluene, benzene, xylenes, mesitylene and the like, halogenated aromatic

hydrocarbons such as chlorobenzene, fluorobenzene and the like, and carboxylic acid amides such as N,N-dimethylformamide and the like, and mixtures thereof. Preferred first solvents include ethers with tetrahydrofuran being more preferred.

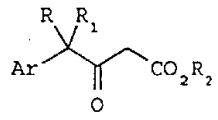
Second and third solvents (which may be the same or different) suitable for use in this invention include, but are not limited to, C_1-C_4alcohols such as methanol, ethanol and the like, and ethers such as tetrahydrofuran, dioxane and the like, and mixtures thereof. Preferred second and third solvents include C_1-C_4alcohols with methanol being more preferred.

Fourth solvents suitable for use in the present invention include, but are not limited to, aromatic hydrocarbons such as toluene, benzene, xylenes, mesitylene and the like, halogenated aromatic hydrocarbons such as chlorobenzene, fluorobenzene and the like, ethers such as tetrahydrofuran, dioxane and the like, carboxylic acid amides such as N,N-dimethylformamide and the like, halogenated aliphatic hydrocarbons such as chloroform, carbon tetrachloride and the like, and acetonitrile, and mixtures thereof.

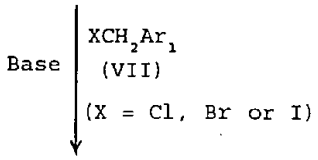
The present invention also includes the novel compounds represented by formulae II, III, IV, and V, wherein Ar, Ar_1, R, R_1 and R_2 are as described hereinabove, provided that in compounds of formula II R is other than hydrogen.

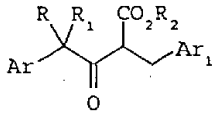
Starting 4-aryl-3-oxobutanoate compounds of formula II may be prepared, as illustrated in Flow Diagram I, by reacting a 4-aryl-3-oxobutanoate of formula VI with a base and a substituted benzyl halide of formula VII.

FLOW DIAGRAM I



(VI)





(II)

Preferred formula I fluoroolefin compounds which may be prepared by the process of this invention are those wherein

R is hydrogen and R_1 is isopropyl or cyclopropyl, or R and R_1 are methyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups; and

Ar_1 is 3-phenoxyphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, 3-biphenyl optionally substituted with up to five groups independently selected from halogen

atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,

3-benzylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or

3-benzoylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups.

The process of the present invention is particularly useful for the preparation of pesticidal fluoroolefins of formula I wherein

R is hydrogen and R_1 is isopropyl or cyclopropyl, or R and R_1 are methyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is 4-chlorophenyl, 4-fluorophenyl, 4-(trifluoromethoxy)phenyl or 4-ethoxyphenyl; and

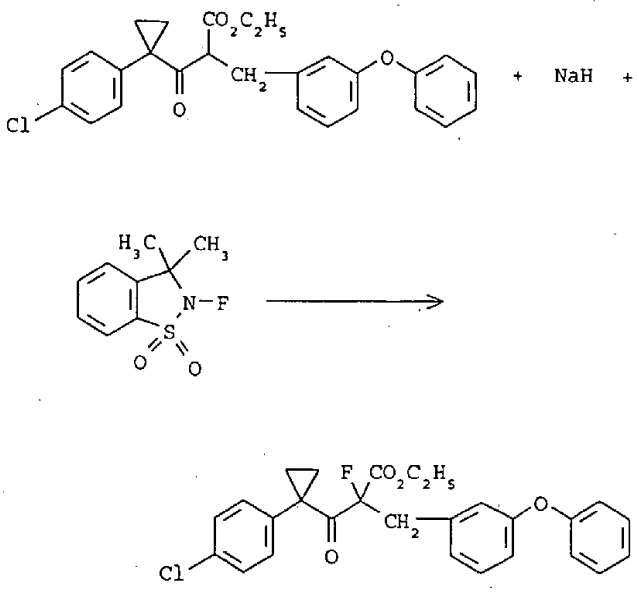
Ar_1 is 4-fluoro-3-phenoxyphenyl or 3-phenoxyphenyl.

Preferred starting formula II compounds of the present invention are those wherein R_2 is C_1-C_4alkyl.

In order to facilitate a further understanding of the invention, the following examples are presented primarily for the purpose of illustrating more specific details thereof. The scope of the invention should not be deemed limited by the examples, but encompasses all of the subject matter defined in the claims.

EXAMPLE 1

Preparation of Ethyl 1-(p-chlorophenyl)-α-fluoro-β-oxo-α-(m-phenoxybenzyl)cyclopropanepropionate

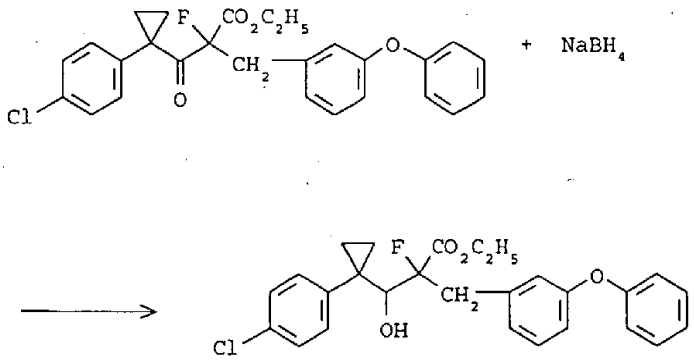


A 60% sodium hydride dispersion in oil (0.17 g, 4.3 mmol) is washed with hexanes, dried and dispersed in tetrahydrofuran. The resultant mixture is cooled with an ice-water bath, treated with a solution of ethyl 1-(*p*-chlorophenyl)-β-oxo-α-(*m*-phenoxybenzyl)cyclopropanepropionate (1.72 g, 3.84 mmol) in tetrahydrofuran, stirred at 0 °C for 4 hours, treated with a solution of N-fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzothiazol-1,1-dioxide (1.10 g, 5.12 mmol) in tetrahydrofuran, stirred at 0 °C for 90 minutes, stirred at room temperature for one hour, cooled in an ice-water bath, quenched with 10 mL of brine, and diluted with ethyl acetate and water.

The organic phase is separated, washed sequentially with water and brine, dried over anhydrous sodium sulfate and concentrated *in vacuo* to obtain a residue. Chromatography of the residue using silica gel and a 19:1 hexanes/ethyl acetate solution gives the title product as a colorless oil (1.25 g, 70%) which is identified by NMR spectral analysis.

EXAMPLE 2

Preparation of Ethyl 1-(p-chlorophenyl)-α-fluoro-β-hydroxy-α-(m-phenoxybenzyl)cyclopropanepropionate, 9:1 [R,S and S,R] to [R,R and S,S] ratio

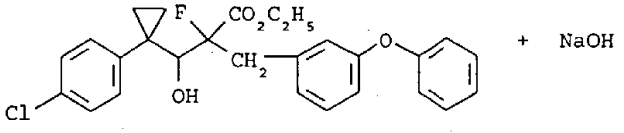


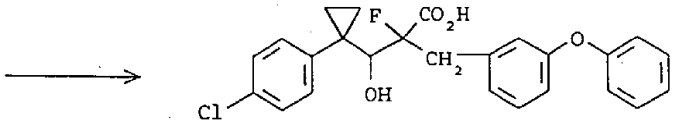
Sodium borohydride (20 mg, 0.53 mmol) is added to a solution of ethyl 1-(*p*-chlorophenyl)-α-fluoro-β-oxo-α-(*m*-phenoxybenzyl)cyclopropanepropionate (214 mg, 0.46 mmol) in methanol at 0 °C. The reaction mixture is stirred at 0 °C for 20 minutes, treated with water (2 mL), and concentrated *in vacuo* to obtain a residue. A solution of the residue in ethyl acetate is washed sequentially with water and brine, dried over anhydrous sodium sulfate, and

concentrated *in vacuo* to give the title product as a colorless gum (224 mg, 100%) which is found to have a 9:1 [R,S and S,R] to [R,R and S,S] ratio by NMR spectral analyses.

EXAMPLE 3

Preparation of 1-(p-chlorophenyl)-α-fluoro-β-hydroxy-α-(m-phenoxybenzyl)cyclopropanepropionic acid, 9:1 [R,S and S,R] to [R,R and S,S] ratio



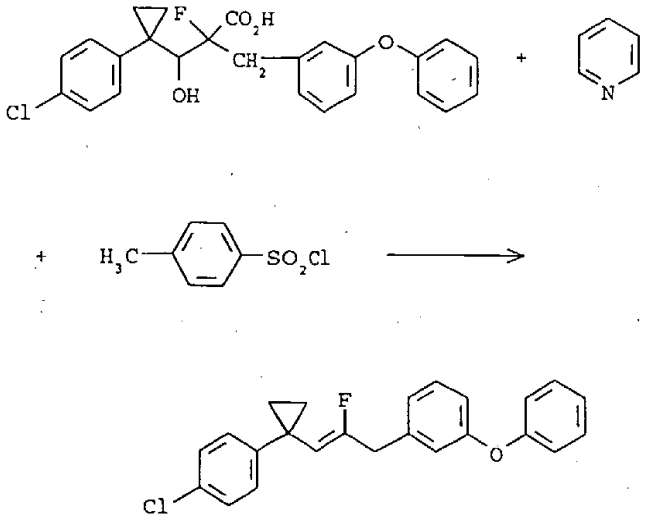


Sodium hydroxide solution (3 mL of a 1 M solution) is added to a solution of ethyl 1-(*p*-chlorophenyl)-α-fluoro-β-hydroxy-α-(m-phenoxybenzyl)cyclopropane-propionate having a 9:1 [R,S and S,R] to [R,R and S,S] ratio (224 mg, 0.48 mmol) in methanol at 0 °C. The reaction mixture is stirred at room temperature overnight, acidified to pH 1 with concentrated hydrochloric acid, and concentrated *in vacuo* to obtain a residue. A solution of the residue in ethyl acetate is washed sequentially with water and brine, dried over

anhydrous sodium sulfate, concentrated *in vacuo*, diluted with diethyl ether and hexanes, and concentrated *in vacuo* to give the title product as a white foam (210 mg, 100%) which is identified by NMR spectral analysis.

EXAMPLE 4

Preparation of 1-(*p*-Chlorophenyl)-1-[2-fluoro-3-(*m*-phenoxyphenyl)propenyl]cyclopropane, (9:1) Z to E ratio

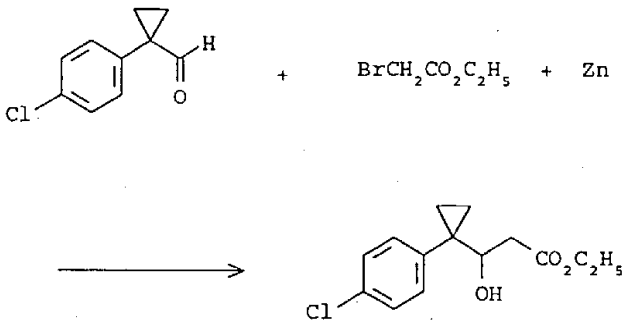


p-Toluenesulfonyl chloride (19.07 mg, 0.10 mmol) is added to a solution of 1-(*p*-chlorophenyl)-α-fluoro-β-hydroxy-α-(*m*-phenoxybenzyl)cyclopropanepropionic acid having a 9:1 [R,S and S,R] to [R,R and S,S] ratio (20 mg, 0.05 mmol) in pyridine (2 mL). The reaction mixture is heated to 60 °C and poured into water. The aqueous mixture is extracted with diethyl ether. The organic extracts are combined, washed sequentially with 2 N

hydrochloric acid, water, 10% sodium hydrogen carbonate solution and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give the title product as a colorless oil (18 mg, 100%) which is found to have a 9:1 Z to E ratio by NMR spectral analyses.

EXAMPLE 5

Preparation of Ethyl 1-(*p*-chlorophenyl)-β-hydroxy-cyclopropanepropionate

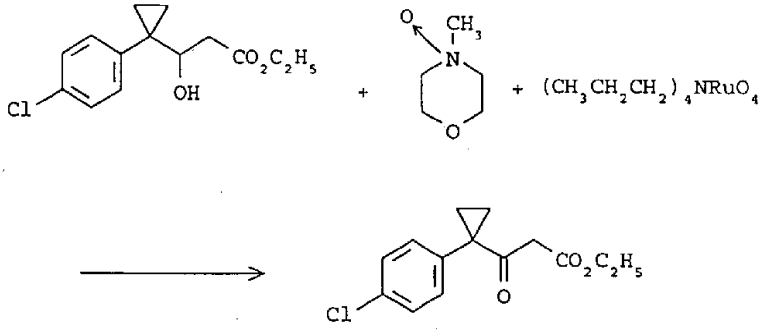


A mixture of zinc dust (4.0 g, 61.2 mmol), ethyl bromoacetate (6.5 mL, 58.3 mmol) and 1-(*p*-chlorophenyl)-cyclopropanecarboxaldehyde (10.0 g, 55.4 mmol) in toluene is stirred at 70 °C for 45 minutes, cooled with an ice-water bath, treated with 100 mL of 10% sulfuric acid, stirred at room temperature for one hour, and diluted with ethyl acetate. The organic phase is separated, washed sequentially with 10% sulfuric acid, water, 10% sodium hydrogen carbonate solution and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to obtain an oil. Chromatography of the oil using silica gel and a 9:1 to 7:3 hexanes/ethyl acetate gradient gives

the title product as a colorless oil (11.3 g, 76%) which is identified by NMR spectral analyses.

EXAMPLE 6

Preparation of Ethyl 1-(p-chlorophenyl)-β-oxo-cyclopropanepropionate

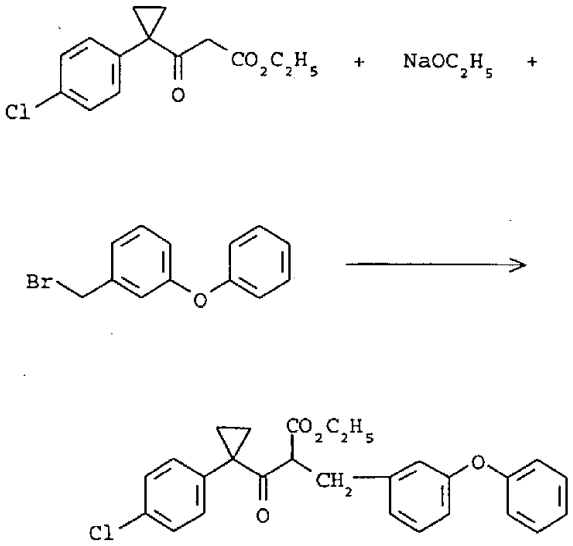


A solution of ethyl 1-(*p*-chlorophenyl)-β-hydroxy-cyclopropanepropionate (7.9 g, 29.4 mmol) and 4-methyl-morpholine N-oxide (14.0 g, 120 mmol) in acetonitrile containing 30 4Å molecular sieves is stirred at room temperature for 20 minutes, treated with tetrapropyl-ammonium perruthenate (0.8 g, 2.3 mmol), stirred for two hours while maintaining the reaction mixture temperature at room temperature with an ice-water bath, diluted with diethyl ether, filtered through diatomaceous earth, and concentrated *in vacuo* to obtain a residue. A solution of the residue in diethyl ether is washed sequentially with water, 5% sulfuric acid, water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to obtain a dark oil. Chromatography of the oil using silica gel and a 1:19 to 3:17 ethyl acetate/hexanes

gradient gives the title product as a pale yellow oil (4.3 g, 55%) which is identified by NMR spectral analyses.

EXAMPLE 7

Preparation of Ethyl 1-(p-chlorophenyl)-β-oxo-α-(m-phenoxybenzyl)cyclopropanepropionate



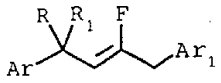
A mixture of sodium (0.31 g, 13.5 mmol) in ethanol (90 mL) is stirred at room temperature until the sodium dissolves. The resultant solution is heated to 70 °C, treated dropwise with a solution of ethyl 1-(*p*-chlorophenyl)-β-oxocyclopropanepropionate (3.4 g, 12.8 mmol) in ethanol, stirred at 70 °C for one hour, treated dropwise with a solution of α-bromo-*m*-tolyl phenyl ether (4.0 g, 15.2 mmol) in ethanol, stirred at reflux overnight,

stirred at room temperature for two days, and concentrated *in vacuo* to obtain a residue. A solution of the residue in ethyl acetate is washed sequentially with water, 10% sodium hydrogen carbonate solution and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to obtain an oil. Chromatography of the oil using silica gel and a 19:1 hexanes/ethyl acetate solution gives the title product as a colorless oil (5.24 g, 92%) which is identified by NMR spectral analysis.

~~CLAIMS~~

The claims defining the invention are as follows:

1. A process for the preparation of a fluoroolefin compound having the structural formula I



(I)

wherein

R is hydrogen or C_1-C_4alkyl, and

R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl or cyclopropyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or

1- or 2-naphthyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

Ar_1 is phenoxyphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,

biphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,

benzylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or

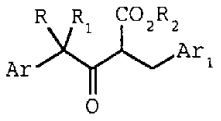
benzoylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

and

the configuration of the groups $ArCRR_1$- and $-CH_2Ar_1$ about the double bond is predominantly mutually trans,

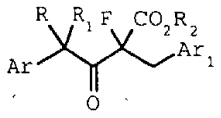
which process comprises

a) fluorinating a 4-aryl-3-oxo-2-(substituted benzyl)butanoate compound having the structural formula II



(II)

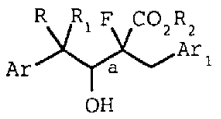
wherein R_2 is C_1-C_6alkyl and Ar, Ar_1, R and R_1 are as described above in the presence of a first base to form a 4-aryl-2-fluoro-3-oxo-2-(substituted benzyl)butanoate compound having the structural formula III



(III)

wherein Ar, Ar_1, R, R_1 and R_2 are as described above;

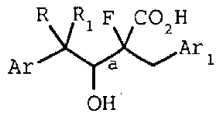
b) reducing the formula III compound to form a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoate compound having the structural formula IV



(IV)

wherein Ar, Ar_1, R, R_1 and R_2 are as described above and the configuration of the groups $ArCRR_1CH(OH)$- and $-CF(CO_2R_2)CH_2Ar_1$ attached to the bond labelled "a" is predominantly R,S or S,R or a mixture thereof;

c) saponifying the formula IV compound to form a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoic acid compound having the structural formula V



(V)

wherein Ar, Ar_1, R and R_1 are as described above and the configuration of the groups $ArCRR_1CH(OH)$- and $-CF(CO_2H)CH_2Ar_1$ attached to the bond labelled "a" is predominantly R,S or S,R or a mixture thereof; and

d) reacting the formula V compound with a sulfonyl halide compound and a second base.

2. The process according to claim 1 wherein the first base is selected from the group consisting of an alkali metal hydroxide, an alkaline earth metal hydroxide,

an alkali metal C_1-C_6alkoxide, an alkaline earth metal C_1-C_6alkoxide, a thallium(I) C_1-C_6alkoxide, thallium(I) hydroxide, an alkali metal hydride, an alkyl lithium and an aryl lithium, and the second base is a tertiary amine selected from the group consisting of a tri-(C_1-C_4alkyl)amine, pyridine and a substituted pyridine.

3. The process according to claim 1 or 2 wherein said fluorinating step comprises reacting the formula II compound with a fluorinating agent selected from the group consisting of fluorine, diethylaminosulfur trifluoride, 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), N-fluoropyridinium pyridine heptafluorodiborate, N-fluorobenzenesulfonimide, N-fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzothiazol-1,1-dioxide and an N-fluoro oxathiazinone dioxide.

4. The process according to any one of claims 1 to 3 wherein said reducing step comprises reacting the formula III compound with a reducing agent selected from the group consisting of a borohydride, a substituted aluminum hydride, an aluminum C_1-C_6alkoxide/C_1-C_6alcohol complex and hydrogen in the presence of a noble metal catalyst.

5. The process according to any one of claims 1 to 4 wherein said saponifying step comprises reacting the formula IV compound with a base selected from the group consisting of an alkali metal carbonate, an alkaline earth metal carbonate, an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkali metal C_1-C_6alkoxide, an alkaline earth metal C_1-C_6alkoxide, thallium(I) carbonate, a thallium(I) C_1-C_6alkoxide and thallium(I) hydroxide.

6. The process according to any one of claims 1 to 5 wherein the sulfonyl halide compound is selected from the group consisting of an alkylsulfonyl chloride and an arylsulfonyl chloride.

7. The process according to any one of claims 1 to 6 wherein

R is hydrogen and R_1 is isopropyl or cyclopropyl, or R and R_1 are methyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

Ar_1 is 3-phenoxyphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,

3-biphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,

3-benzylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or

3-benzoylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups; and

R_2 is C_1-C_4alkyl.

8. The process according to claim 7 wherein Ar is 4-chlorophenyl, 4-fluorophenyl, 4-(trifluoromethoxy) phenyl or 4-ethoxyphenyl; and Ar_1 is 4-fluoro-3-phenoxyphenyl or 3-phenoxyphenyl.

9. A process according to claim 7 or 8 wherein:

the second base is a tertiary amine selected from the group consisting of a tri(C_1-C_4alkyl)amine, pyridine and a substituted pyridine;

said fluorinating step comprises reacting the formula II compound with at least about one molar equivalent of a fluorinating agent selected from the group consisting of fluorine, diethylaminosulfur trifluoride, 1-fluoro-4-hydroxy-1,4-diazonia-bicyclo[2.2.2]octane bis(tetrafluoroborate), N-fluoropyridinium pyridine heptafluorodiborate, N-fluorobenzenesulfonimide, N-fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzothiazol-1,1-dioxide and an N-fluoro oxathiazinone dioxide, in the presence of at least about one molar equivalent of the first base, which is selected from the group consisting of an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkali metal C_1-C_6alkoxide, an alkaline earth metal C_1-C_6alkoxide, a thallium(I) C_1-C_6alkoxide, thallium(I) hydroxide, an alkali metal hydride, an alkyl lithium and an aryl lithium, in the presence of a first solvent, at a temperature in the approximate range of -15°C to 100°C;

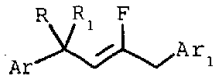
said reducing step comprises reacting the formula III compound with at least one molar equivalent of a reducing agent selected from the group consisting of a borohydride, a substituted aluminum hydride, an aluminum C_1-C_6alkoxide/C_1-C_6alcohol complex, and hydrogen in the presence of a noble metal

catalyst, at a temperature in the approximate range of -50°C to 80°C, in the presence of a second solvent;

said saponifying step comprises reacting the formula IV compound with at least about one molar equivalent of a base selected from the group consisting of an alkali metal carbonate, an alkaline earth metal carbonate, an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkali metal C_1-C_6alkoxide, an alkaline earth metal C_1-C_6alkoxide, thallium(I) carbonate, a thallium(I) C_1-C_6alkoxide and thallium(I) hydroxide, followed by at least about one molar equivalent of an acid, at a temperature in the approximate range of -15°C to 80°C, in the presence of a third solvent; and

said reaction with the sulfonyl halide compound includes at least about one molar equivalent of a sulfonyl halide compound selected from the group consisting of an alkylsulfonyl chloride and an arylsulfonyl chloride, and at least one molar equivalent of a second base acid, at a temperature in the approximate range of 0°C to 130°C, in the presence of a fourth solvent.

10. A process for the preparation of a fluoroolefin compound having the structural formula I



(I)

wherein

R is hydrogen or C_1-C_4alkyl, and

R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl or cyclopropyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

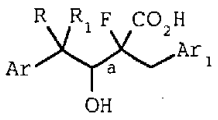
Ar is phenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or 1- or 2-naphthyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

Ar_1 is phenoxyphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, biphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, benzylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or benzoylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups; and

the configuration of the groups $ArCRR_1$- and $-CH_2Ar_1$ about the double bond is predominantly mutually trans,

which process comprises

reacting a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoic acid compound having the structural formula V

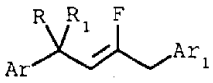


(V)

wherein Ar, Ar_1, R and R_1 are as described above and the configuration of the groups $ArCRR_1CH(OH)$- and $-CF(CO_2H)CH_2AR_1$ attached to the bond labelled "a" is predominantly R,S or S,R or a mixture thereof with a sulfonyl halide compound and a base.

11. The process according to claim 10 wherein the sulfonyl halide compound is selected from the group consisting of an alkylsulfonyl chloride and an arylsulfonyl chloride, and the base is a tertiary amine.

12. A process for the preparation of a fluoroolefin compound having the structural formula I



(I)

wherein

R is hydrogen or C_1-C_4alkyl, and

R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl or cyclopropyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with up to three groups independently selected from halogen atoms,

C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or 1- or 2-naphthyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

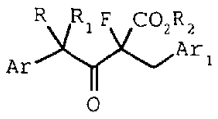
Ar_1 is phenoxyphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, biphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, benzylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or benzoylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

and

the configuration of the groups $ArCRR_1$- and $-CH_2Ar_1$ about the double bond is predominantly mutually trans,

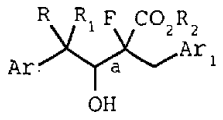
which process comprises

a) reducing a 4-aryl-2-fluoro-3-oxo-2-(substituted benzyl)butanoate compound having the structural formula III



(III)

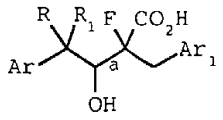
wherein R_2 is C_1-C_6alkyl and Ar, Ar_1, R and $R_1$are as described above to form a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoate compound having the structural formula IV



(IV)

wherein Ar, Ar_1, R, R_1 and R_2 are as described above and the configuration of the groups $ArCRR_1CH(OH)$- and $-CF(CO_2R_2)CH_2Ar_1$ attached to the bond labelled "a" is predominantly R,S or S,R or a mixture thereof;

b) saponifying the formula IV compound to form a 4-aryl-2-fluoro-3-hydroxy-2-(substituted benzyl)butanoic acid compound having the structural formula V



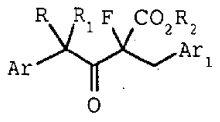
(V)

wherein Ar, Ar_1, R and R_1 are as described above and the configuration of the groups $ArCRR_1CH(OH)$- and $-CF(CO_2H)CH_2Ar_1$ attached to the bond labelled "a" is predominantly R,S or S,R or a mixture thereof; and

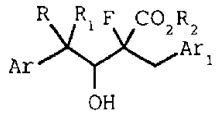
c) reacting the formula V compound with a sulfonyl halide compound and a base.

13. The process according to claim 12 wherein: said reducing step comprises reacting the formula III compound with a reducing agent selected from the group consisting of a borohydride, a substituted aluminum hydride, an aluminum C_1-C_6alkoxide/C_1-C_6alcohol complex and hydrogen in the presence of a noble metal catalyst; said saponifying step comprises reacting the formula IV compound with a base selected from the group consisting of an alkali metal carbonate, an alkaline earth metal carbonate, an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkali metal C_1-C_6alkoxide, an alkaline earth metal C_1-C_6alkoxide, thallium(I) carbonate, a thallium(I) C_1-C_6alkoxide and thallium(I) hydroxide; the sulfonyl halide compound is selected from the group consisting of an alkylsulfonyl chloride and an arylsulfonyl chloride; and the base is a tertiary amine.

14. A compound having the structural formula

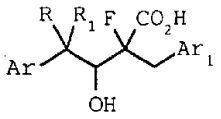


(III)



(IV)

or



(V)

wherein

R is hydrogen or C_1-C_4alkyl, and

R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl or cyclopropyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or 1- or 2-naphthyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

Ar_1 is phenoxyphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, biphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, benzylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or benzoylphenyl optionally substituted with up to five groups independently selected from halogen

atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

and

R_2 is C_1-C_6alkyl; and

the optical isomers and diastereomers thereof.

15. The compound according to claim 14 wherein

R is hydrogen and R_1 is isopropyl or cyclopropyl, or R and R_1 are methyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

Ar_1 is 3-phenoxyphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,

3-biphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,

3-benzylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or

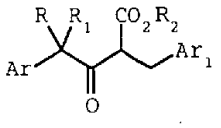
3-benzoylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

and

R_2 is C_1-C_4alkyl.

16. The compound according to claim 15 wherein
Ar is 4-chlorophenyl, 4-fluorophenyl, 4-(trifluoromethoxy)phenyl or 4-ethoxyphenyl; and
Ar_1 is 4-fluoro-3-phenoxyphenyl or 3-phenoxyphenyl.

17. A compound having the structural formula II



(II)

wherein
R is C_1-C_4alkyl, and
R_1 is C_1-C_4alkyl, C_1-C_4haloalkyl or cyclopropyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;
Ar is phenyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or
1- or 2-naphthyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;
Ar_1 is phenoxyphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,
biphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups,
benzylphenyl optionally substituted with up to

five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or benzoylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups; and

R_2 is C_1-C_6alkyl; and

the optical isomers thereof.

18. The compound according to claim 17 wherein

R and R_1 are methyl, or R and R_1 are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with up to three groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups;

Ar_1 is 3-phenoxyphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, 3-biphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, 3-benzylphenyl optionally substituted with up to five groups independently selected from halogen atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups, or 3-benzoylphenyl optionally substituted with up to five groups independently selected from halogen

atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups; and

R_2 is C_1-C_4alkyl.

19. The compound according to claim 18 wherein Ar is 4-chlorophenyl, 4-fluorophenyl, 4-(trifluoromethoxy)phenyl or 4-ethoxyphenyl; and

Ar_1 is 4-fluoro-3-phenoxyphenyl or 3-phenoxyphenyl.

20. A process as claimed in claim 1, carried out substantially as described herein with reference to Examples 1 to 4.

21. A process as claimed in claim 10, carried out substantially as described herein with reference to Example 4.

22. A fluoroolefin compound having the structural formula I whenever prepared by a process as claimed in any one of claims 1 to 13, 20 and 21.

23. Use of a compound as claimed in claim 22 as a pesticide.

24. A pesticidal composition containing a compound as claimed in claim 22 as pesticidal agent.

atoms, C_1-C_4alkyl groups, C_1-C_4haloalkyl groups, C_1-C_4alkoxy groups or C_1-C_4haloalkoxy groups; and

R_2 is C_1-C_4alkyl.

19. The compound according to claim 18 wherein Ar is 4-chlorophenyl, 4-fluorophenyl, 4-(trifluoromethoxy)phenyl or 4-ethoxyphenyl; and Ar_1 is 4-fluoro-3-phenoxyphenyl or 3-phenoxyphenyl.

20. A process as claimed in claim 1, carried out substantially as described herein with reference to Examples 1 to 4.

21. A process as claimed in claim 10, carried out substantially as described herein with reference to Example 4.

22. A fluoroolefin compound having the structural formula I whenever prepared by a process as claimed in any one of claims 1 to 13, 20 and 21.

23. Use of a compound as claimed in claim 22 as a pesticide.

24. A pesticidal composition containing a compound as claimed in claim 22 as pesticidal agent.

DATED this EIGHTEENTH day of JUNE 1998

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Patent Attorneys for the Applicant
SPRUSON & FERGUSON