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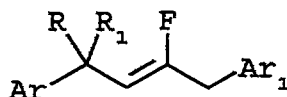
PROCESS AND INTERMEDIATE COMPOUNDS FOR THE
PREPARATION OF PESTICIDAL FLUOROOLEFIN COMPOUNDS

BACKGROUND OF THE INVENTION

Fluoroolefin compounds which are useful as
5 pesticidal agents are described in WO 94/06741 and GB
2,288,803-A. Those references also describe processes
for the preparation of fluoroolefin compounds. However,
those processes are not entirely satisfactory because the
fluoroolefin compounds are produced in relatively low
10 yields. Those references also fail to teach how to make
the intermediate compounds of the present invention.

SUMMARY OF THE INVENTION

The present invention provides an effective and
15 efficient process for the preparation of a pesticidal
fluoroolefin compound having the structural formula I



(I)

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wherein

R is hydrogen or C₁-C₄alkyl, and

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R₁ is C₁-C₄alkyl or cyclopropyl, or R and R₁ are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with any combination
5 of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups, or

1- or 2-naphthyl optionally substituted with any combination of from one to three halogen,
10 C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups;

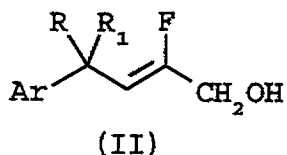
Ar₁ is phenoxyphenyl optionally substituted with any combination of from one to five halogen,
15 C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups,

biphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups,

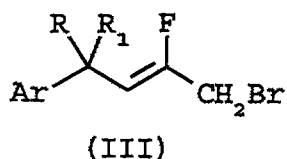
20 benzylphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups, or

25 benzoylphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups; and

the configuration of the groups ArCRR₁- and -CH₂Ar₁ about the double bond is predominately mutually trans,
30 which process comprises reacting a 4-aryl-2-fluoro-2-butene-1-ol compound having the structural formula II

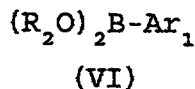
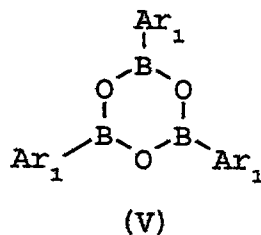
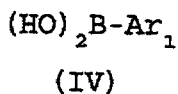


wherein Ar, R and R₁ are as described above, with a brominating agent to form a 4-aryl-1-bromo-2-fluoro-2-butene compound having the structural formula III



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wherein Ar, R and R₁ are as described above, and reacting the formula III compound with a palladium catalyst, a base, and a boronic acid having the structural formula IV, a boronic anhydride having the structural formula V or a borate ester having the structural formula VI



wherein R₂ is C₁-C₄alkyl and Ar₁ is as described above.

The present invention also relates to the intermediate 4-aryl-1-bromo-2-fluoro-2-butene compounds of formula III.

5 It is, therefore, an object of the present invention to provide an effective and efficient process for the preparation of pesticidal fluoroolefin compounds.

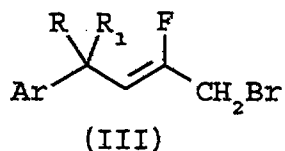
It is also an object of the present invention to provide intermediate compounds which are useful for the preparation of pesticidal fluoroolefin compounds.

10 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.

DETAILED DESCRIPTION OF THE INVENTION

A preferred embodiment of the present invention
15 comprises reacting a 4-aryl-2-fluoro-2-butene-1-ol of formula II with at least about one molar equivalent of a brominating agent, preferably in a temperature range of about 50 °C to 130 °C, in the presence of a first solvent to form a 4-aryl-1-bromo-2-fluoro-2-butene of formula
20 III, and reacting the formula III compound with about 0.001 to 0.1, preferably about 0.005 to 0.1, molar equivalent of a palladium catalyst, at least about 2 molar equivalents, preferably about 2-6 molar equivalents of a base, and a boronic acid of formula IV, preferably 1
25 molar equivalent of a boronic acid in a temperature range of about 50 °C to 130 °C, in the presence of a second solvent.

The present invention also relates to the 4-aryl-1-bromo-2-fluoro-2-butene compounds which are utilized in
30 the process of this invention. The 4-aryl-1-bromo-2-fluoro-2-butene compounds have the structural formula III



wherein

R is hydrogen or C₁-C₄alkyl, and

R₁ is C₁-C₄alkyl or cyclopropyl, or R and R₁ are taken

5 together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups, or

10

1- or 2-naphthyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups; and

15 the configuration of the groups ArCRR₁- and -CH₂Br about the double bond is predominately mutually trans.

Exemplary of halogen hereinabove are fluorine, chlorine, bromine and iodine. The terms "C₁-C₄haloalkyl" and "C₁-C₄haloalkoxy" are defined as a C₁-C₄alkyl group and a C₁-C₄alkoxy group substituted with one or more halogen atoms, respectively.

20

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.

25

Brominating agents suitable for use in the process of this invention include, but are not limited to, bromine/triphenyl phosphine complexes, phosphorus tribromide, thionyl bromide, concentrated hydrobromic

30

acid, and the like, and mixtures thereof. Bromine/tri-phenyl phosphine complexes are preferred brominating agents.

First 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, carboxylic acid amides such as N,N-dimethyl-
10 formamide and the like, ethers such as tetrahydrofuran, dioxane and the like, and halogenated hydrocarbons such as chloroform, carbon tetrachloride and the like, and mixtures thereof. Preferred first solvents include halogenated hydrocarbons with carbon tetrachloride being
15 more preferred.

Second solvents useful in the process of this invention include, but are not limited to, aromatic hydrocarbons such as toluene, benzene, xylenes, mesitylene and the like, halogenated aromatic hydro-
20 carbons such as chlorobenzene, fluorobenzene and the like, carboxylic acid amides such as N,N-dimethylformamide and the like, glycols such as dimethoxyethane and the like, C₁-C₄alcohols such as methanol, ethanol and the like, ketones such as acetone and the like, and ethers
25 such as tetrahydrofuran, dioxane and the like, and mixtures thereof, and mixtures with water. Preferred second solvents include aromatic hydrocarbons and aromatic hydrocarbon/C₁-C₄alcohol mixtures with a toluene/ethanol mixture being more preferred.

30 Palladium catalysts suitable for use in the present invention include, but are not limited to, palladium(0) catalysts such as bis(dibenzylideneacetone)palladium(0), tetrakis(triphenylphosphine)palladium(0) and the like, palladium(II) catalysts such as bis(acetonitrile)-
35 palladium(II) chloride, bis(triphenylphosphine)-

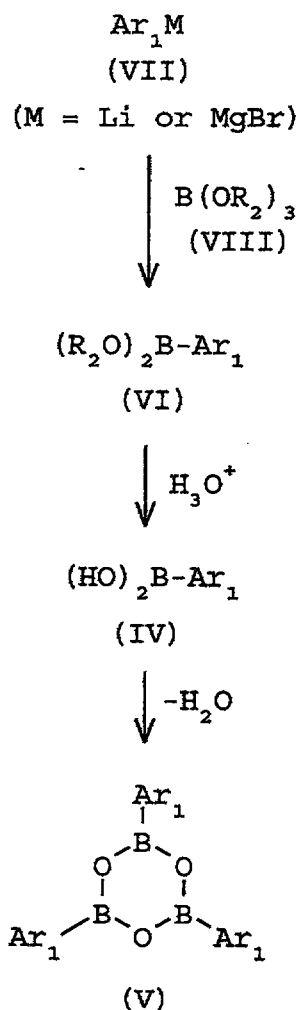
palladium(II) chloride, [1,4-bis(diphenylphosphine)-
butane]palladium(II) dichloride, [1,1'-bis(diphenyl-
phosphino)ferrocene]palladium(II) diacetate,
palladium(II) acetate, palladium(II) chloride and the
5 like, and palladium on activated carbon, and mixtures
thereof. Preferred catalysts include palladium(0)
catalysts with bis(dibenzylideneacetone)palladium(0)
being more preferred.

Bases suitable for use in this invention include,
10 but are not limited to, alkali metal carbonates such as
sodium carbonate and potassium carbonate, alkaline earth
metal carbonates such as calcium carbonate and the like,
alkali metal hydrogen carbonates such as sodium hydrogen
carbonate and the like, alkali metal hydroxides such as
15 sodium hydroxide and potassium hydroxide, alkaline earth
metal hydroxides such as calcium hydroxide and the like,
alkali metal C₁-C₆alkoxides such as potassium tert-
butoxide and the like, thallium(I) carbonate, thallium(I)
C₁-C₆alkoxides, thallium(I) hydroxide, and
20 tri(C₁-C₄alkyl)amines such as trimethylamine, and mixtures
thereof. Preferred bases include alkali metal carbonates
with potassium carbonate being more preferred.

In another preferred embodiment of the present
invention, a 4-aryl-1-bromo-2-fluoro-2-butene of formula
25 III is reacted with a palladium catalyst, a base and a
boronic acid of formula IV.

Boronic acids of formula IV, boronic anhydrides of
formula V, and borate esters of formula VI may be
prepared, as illustrated in Flow Diagram I, by reacting
30 an aryl compound of formula VII with a tri(C₁-C₄alkyl)
borate of formula VIII to form the formula VI borate
ester, and hydrolyzing the formula VI borate ester with
aqueous acid to form the boronic acid of formula IV which
may spontaneously combine with other formula IV compounds
35 to form the boronic anhydride of formula V.

FLOW DIAGRAM I



Starting 4-aryl-2-fluoro-2-butene-1-ol compounds of formula II may be prepared according to the procedures described in WO 94/06741 and GB 2,288,803-A.

- 5 In another preferred embodiment of the present invention, a 4-aryl-2-fluoro-2-butene-1-ol of formula II is reacted with a brominating agent in a temperature range of about 50 °C to 130 °C, and a 4-aryl-1-bromo-2-fluoro-2-butene of formula III is reacted with a
- 10 palladium catalyst, a base and a formula IV, V or VI compound in a temperature range of about 50 °C to 130 °C.

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

5 R is hydrogen and R₁ is isopropyl or cyclopropyl, or R and R₁ are methyl, or R and R₁ are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, 10 C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups; and

Ar₁ is 3-phenoxyphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or 15 C₁-C₄haloalkoxy groups,

3-biphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups,

20 3-benzylphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups, or

25 3-benzoylphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups.

The process of the present invention is also preferably used for the preparation of pesticidal 30 fluoroolefins of formula I wherein

R and R₁ are methyl, or R and R₁ are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

35 Ar is phenyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl,

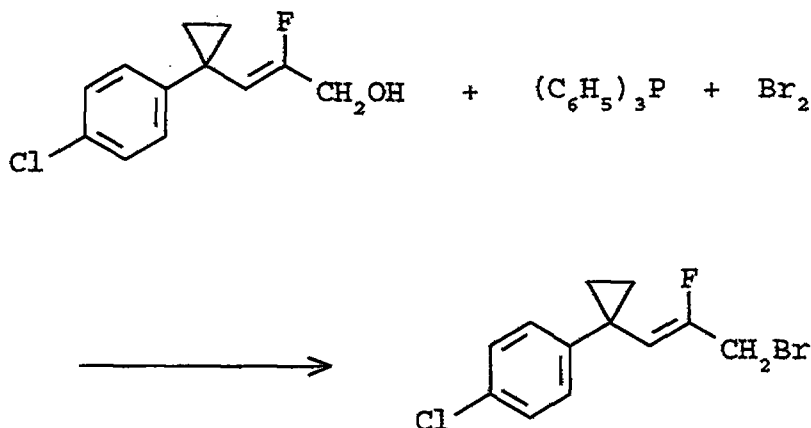
C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups;
and

Ar₁ is 3-phenoxyphenyl optionally substituted with any
combination of from one to five halogen, C₁-C₄alkyl,
5 C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups.

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
10 be deemed limited by the examples, but encompasses all
the subject matter defined in the claims.

EXAMPLE 1

Preparation of 1-(p-Chlorophenyl)-1-(3-bromo-2-
15 fluoropropenyl)cyclopropane, (Z)-



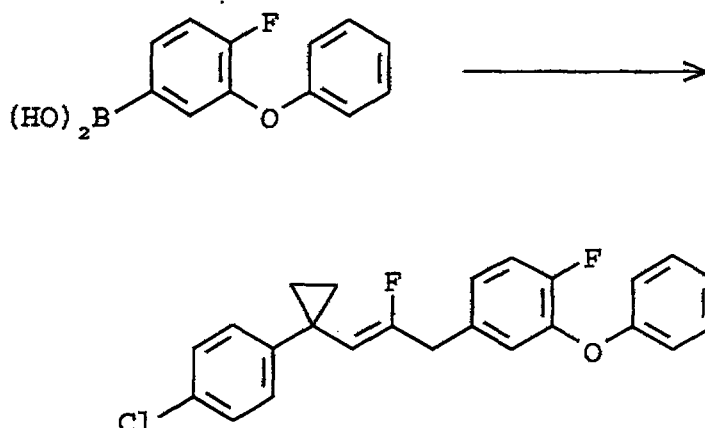
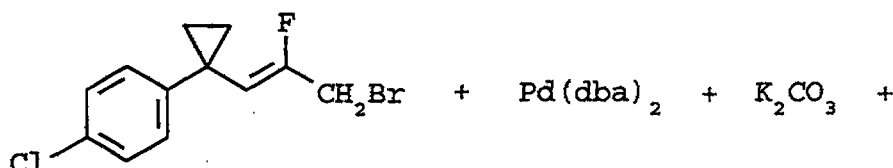
Under a nitrogen atmosphere, a solution of bromine
(0.767 g, 4.8 mmol) in carbon tetrachloride at ice-water
bath temperature is treated sequentially with a solution
20 of triphenylphosphine (1.26 g, 4.8 mmol) in carbon
tetrachloride and a solution of 3-[1-(p-chlorophenyl)-
cyclopropyl]-2-fluoro-2-propen-1-ol, (Z)- (0.907 g, 4
mmol) in carbon tetrachloride, heated to and stirred at
reflux for 70 minutes, cooled to room temperature, and

poured into petroleum ether. The resultant mixture is filtered, and the filtrate is concentrated *in vacuo* to obtain a residue. The residue is dissolved in petroleum ether and passed through a plug of silica gel (eluted
5 with hexanes) to obtain an oil. Flash column chromatography of the oil using silica gel and a 3:20 methylene chloride/hexanes solution gives the title product as a colorless oil (0.73 g, 63% yield) which is identified by NMR spectral analyses.

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EXAMPLE 2

Preparation of 1-(p-Chlorophenyl)-1-[2-fluoro-3-(4-fluoro-3-phenoxyphenyl)propenyl]cyclopropane, (Z)-



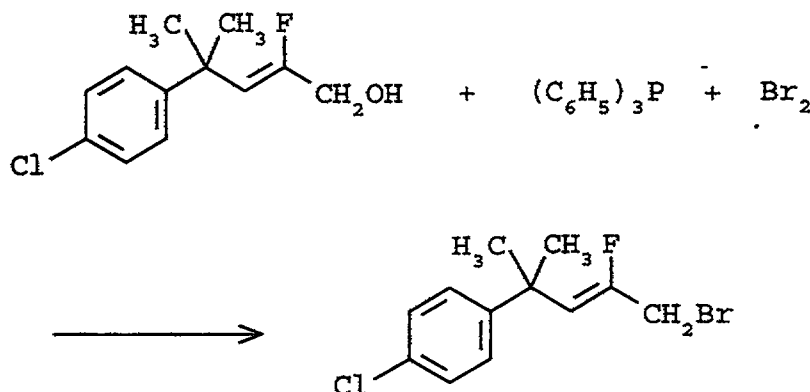
Under a nitrogen atmosphere, a mixture of 1-(p-chlorophenyl)-1-(3-bromo-2-fluoropropenyl)cyclopropane,
15 (Z)- (0.434 g, 1.5 mmol), 4-fluoro-3-phenoxybenzeneboronic acid (0.452 g, 1.95 mmol), potassium carbonate

(1.86 g, 13.5 mmol) and bis(dibenzylideneacetone)-
palladium(0) ($\text{Pd}(\text{dba})_2$, 4.3 mg, 0.075 mmol) in toluene is
heated at 80 °C for one hour, cooled to room temperature,
diluted with water, and filtered through diatomaceous
5 earth. The phases are separated and the aqueous phase is
extracted with ethyl acetate. The organic phase and
ethyl acetate extract are combined, washed with water,
dried over anhydrous sodium sulfate and concentrated in
vacuo to obtain a residue. Flash column chromatography
10 of the residue using silica gel and a 3:20 methylene
chloride/hexanes solution gives the title product as an
oil (0.274 g, 63% yield) which is identified by NMR
spectral analyses.

As can be seen from the data in Examples 1 and 2,
15 1-(p-chlorophenyl)-1-[2-fluoro-3-(4-fluoro-3-phenoxy-
phenyl)propenyl]cyclopropane, (Z)- is obtained in 40%
yield from 3-[1-(p-chlorophenyl)cyclopropyl]-2-fluoro-2-
propen-1-ol, (Z)-. In contrast, WO 94/06741 discloses
that 1-(p-chlorophenyl)-1-[2-fluoro-3-(4-fluoro-3-
20 phenoxyphenyl)propenyl]cyclopropane, (Z)- is obtained in
20% yield from 3-[1-(p-chlorophenyl)cyclopropyl]-2-
fluoro-2-propen-1-ol, (Z)-.

EXAMPLE 3

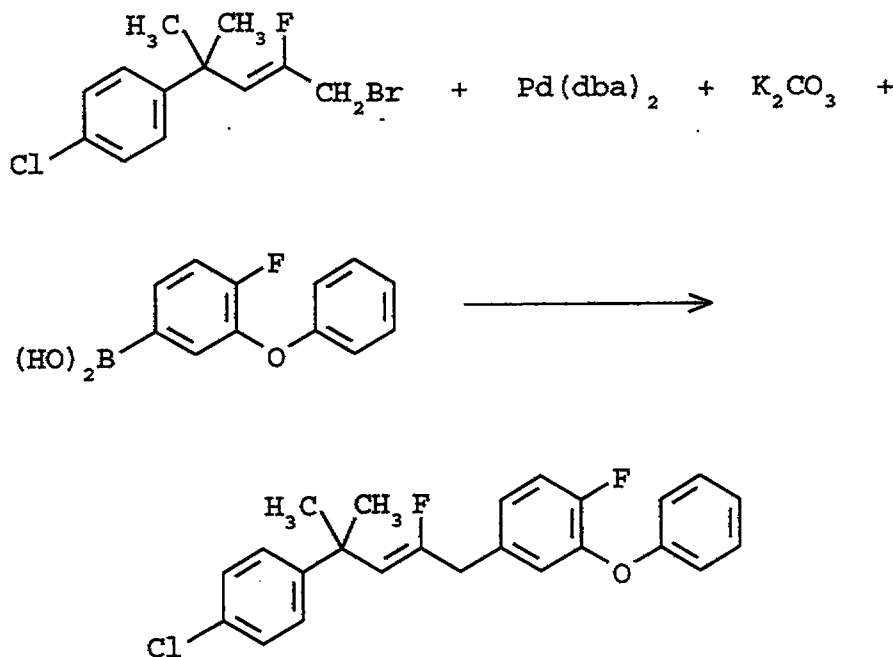
Preparation of 1-Bromo-4-(p-chlorophenyl)-2-fluoro-4-methyl-2-pentene, (Z)-



- 5 Under a nitrogen atmosphere, a solution of triphenyl phosphine (0.96 g, 4.25 mmol) in carbon tetrachloride at -5 °C is treated dropwise with a solution of bromine (0.679 g, 4.25 mmol) in carbon tetrachloride, warmed to and stirred at room temperature for 45 minutes, treated
- 10 with a solution of 4-(p-chlorophenyl)-2-fluoro-4-methyl-2-penten-1-ol, (Z)- (0.81 g, 3.54 mmol) in carbon tetrachloride, refluxed for 2 hours, cooled to room temperature, and poured into petroleum ether. The resultant mixture is filtered through diatomaceous earth.
- 15 The filtrate is washed sequentially with water, saturated sodium hydrogen carbonate solution and brine, dried over anhydrous sodium sulfate and concentrated *in vacuo* to obtain an oil. Flash column chromatography of the oil using silica gel and a 1:9 ethyl acetate/hexanes solution
- 20 gives the title product as a colorless oil (0.736 g, 71% yield) which is identified by NMR spectral analyses.

EXAMPLE 4

Preparation of 4-(p-Chlorophenyl)-2-fluoro-1-(4-fluoro-3-phenoxyphenyl)-4-methyl-2-pentene, (Z)-



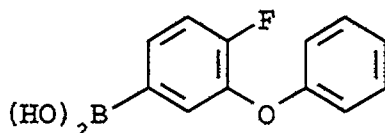
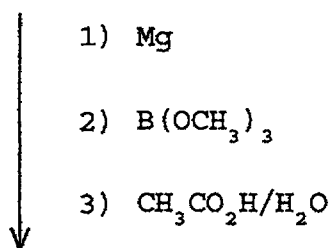
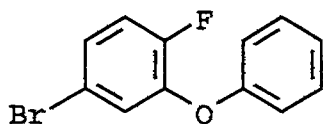
- 5 Under a nitrogen atmosphere, a mixture of 1-bromo-4-(p-chlorophenyl)-2-fluoro-4-methyl-2-pentene, (Z)- (320.8 mg, 1.1 mmol), bis(dibenzylideneacetone)palladium(0) (Pd(dba)_2 , 31.6 mg, 0.055 mmol) in toluene (8 mL) is treated with potassium carbonate (608 mg, 4.4 mmol),
- 10 degassed, treated with a solution of 4-fluoro-3-phenoxybenzeneboronic acid (331.8 mg, 1.43 mmol) in ethanol (2 mL), refluxed for 45 minutes, cooled to room temperature, and filtered through diatomaceous earth. The filtrate is diluted with ethyl acetate, and the
- 15 resultant solution is washed sequentially with water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to obtain a residue. Flash column chromatography of the residue using silica gel and a 1:9 ethyl acetate/hexanes solution gives the title product as

a colorless liquid (401 mg, 91% yield) which is identified by NMR spectral analyses.

As can be seen from the data in Examples 3 and 4, 4-(p-chlorophenyl)-2-fluoro-1-(4-fluoro-3-phenoxyphenyl)-4-methyl-2-pentene, (Z)- is obtained in 65% yield from 4-(p-chlorophenyl)-2-fluoro-4-methyl-2-penten-1-ol, (Z)-. In contrast, GB 2,288,803-A discloses that 4-(p-chlorophenyl)-2-fluoro-1-(4-fluoro-3-phenoxyphenyl)-4-methyl-2-pentene, (Z)- is obtained in 37% yield from 4-(p-chlorophenyl)-2-fluoro-4-methyl-2-penten-1-ol, (Z)-.

EXAMPLE 5

Preparation of 4-Fluoro-3-phenoxybenzeneboronic acid



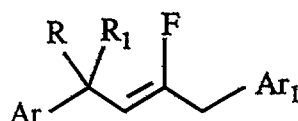
A solution of 5-bromo-2-fluorophenyl phenyl ether (8.01 g, 3 mmol) in tetrahydrofuran is added dropwise to a mixture of magnesium turnings (0.0802 g, 3.3 mmol), a crystal of iodine and a few drops of 1,2-dibromoethane in tetrahydrofuran at 50-55 °C under nitrogen. After the addition is complete, the reaction mixture is stirred at

50-55 °C for 70 minutes and cooled to room temperature. The cooled mixture is added over 25 minutes to a solution of trimethyl borate (4.09 mL, 3.6 mmol) in diethyl ether at dry-ice/acetone bath temperature. After the addition
5 is complete, the mixture is stirred at dry-ice/acetone bath temperature for 20 minutes, allowed to warm to -10 °C over 25 minutes, diluted sequentially with acetic acid and water, stirred at room temperature for 30 minutes, and extracted with ether. The organic extract is washed
10 with water, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to obtain a residue. A mixture of the residue in water is heated over a steam bath for 30 minutes, cooled to room temperature and filtered to obtain a solid which is washed with hexanes and dried to
15 give the title product as a colorless solid (5.7 g, mp 177-180 °C, 82% yield).

-17-

CLAIMS

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



(I)



wherein

R is hydrogen or C₁-C₄alkyl, and

R₁ is C₁-C₄alkyl or cyclopropyl, or R and R₁ are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups, or

1- or 2-naphthyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups;

Ar₁ is phenoxyphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups,

biphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups,

benzylphenyl optionally substituted with any combination of from one to five halogen,

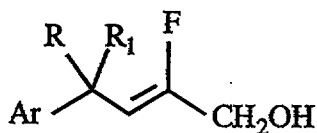
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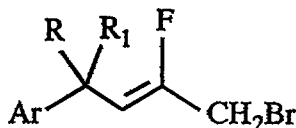
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C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups, or benzoylphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups; and the configuration of the groups ArCRR₁- and -CH₂Ar₁ about the double bond is predominately mutually trans, which process comprises reacting a 4-aryl-2-fluoro-2-butene-1-ol compound having the structural formula II



(II)

wherein Ar, R and R₁ are as described above with a brominating agent to form a 4-aryl-1-bromo-2-fluoro-2-butene compound having the structural formula III



(III)

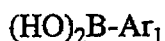
wherein Ar, R and R₁ are as described above, and reacting the formula III compound with a palladium catalyst, a base, and a boronic acid having the structural formula IV, a boronic anhydride having the structural formula V or a borate ester having the structural formula VI

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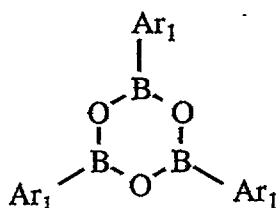


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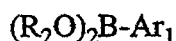
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(IV)



(V)



(VI)



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wherein R_2 is C_1 - C_4 alkyl and Ar_1 is as described above.

2. The process according to claim 1 wherein the brominating agent is a bromine/triphenylphosphine complex.

3. The process according to claim 1 or 2 wherein the palladium catalyst is selected from the group consisting of bis(dibenzylideneacetone)palladium(0), tetrakis(triphenylphosphine)palladium(0), bis(acetonitrile)palladium(II) chloride, bis(triphenylphosphine)palladium(II) chloride, [1,4-bis(diphenylphosphine)butane]palladium(II) dichloride, [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) diacetate, palladium(II) acetate, palladium(II) chloride and palladium on activated carbon and mixtures thereof; and the base is selected from the group consisting of an alkali metal carbonate, an alkaline earth metal carbonate, an alkali metal hydrogen carbonate, an alkali

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ACY-33267-AU, SG, ZA



-20-

metal hydroxide, an alkaline earth metal hydroxide, an alkali metal C₁-C₆alkoxide, thallium(I) carbonate, a thallium(I) C₁-C₆alkoxide, thallium(I) hydroxide and a tri(C₁-C₄alkyl)amine and mixtures thereof.

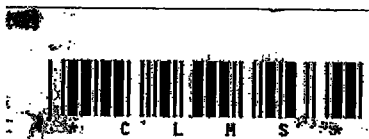
4. The process according to claim 3 wherein the palladium catalyst is bis(dibenzylideneacetone)palladium(0) and the base is an alkali metal carbonate.

5. The process according to any preceding claim wherein the formula III compound is reacted with a boronic acid.

6. The process according to any preceding claim wherein the first reaction step is carried out in a first solvent selected from the group consisting of an aromatic hydrocarbon, a halogenated aromatic hydrocarbon, a carboxylic acid amide, an ether and a halogenated hydrocarbon and mixtures thereof; and the last reaction step is carried out in a second solvent selected from the group consisting of an aromatic hydrocarbon, a halogenated aromatic hydrocarbon, a carboxylic acid amide, a glycol, a C₁-C₄alcohol, a ketone and an ether and mixtures thereof and mixtures with water.

7. The process according to claim 6 wherein the first solvent is a halogenated hydrocarbon and the second solvent is toluene or a toluene/ethanol mixture.

8. The process according to any preceding claim wherein the formula II compound is reacted with the brominating agent at a temperature of about 50°C to 130°C, and the formula III compound is reacted with the palladium



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-21-

catalyst, the base and the formula IV, V or VI compound at a temperature of about 50°C to 130°C.

9. The process according to claim 1 wherein
R is hydrogen and R₁ is isopropyl or cyclopropyl, or R and R₁ are methyl, or R and R₁ are taken together with the carbon atom to which they are attached to form a cyclopropyl group;
Ar is phenyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups; and
Ar₁ is 3-phenoxyphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups,
3-biphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups,
3-benzylphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups, or
3-benzoylphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups.

10. The process according to claim 9 wherein
R and R₁ are methyl, or R and R₁ are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

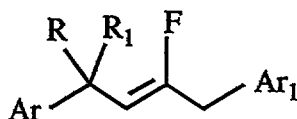
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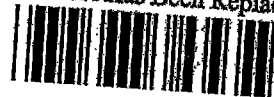
Ar is phenyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups; and
 Ar₁ is 3-phenoxyphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups.

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



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wherein

R is hydrogen or C₁-C₄alkyl, and

R₁ is C₁-C₄alkyl or cyclopropyl, or R and R₁ are taken together with the carbon atom to which they are attached to form a cyclopropyl group;

Ar is phenyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups, or

1- or 2-naphthyl optionally substituted with any combination of from one to three halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups;

Ar₁ is phenoxyphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups,

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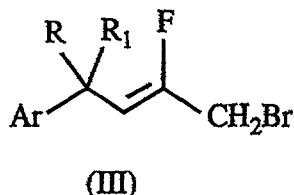
-23-

biphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups,

benzylphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups, or

benzoylphenyl optionally substituted with any combination of from one to five halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄haloalkoxy groups; and

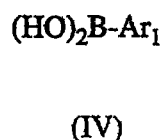
the configuration of the groups ArCRR₁- and -CH₂Ar₁ about the double bond is predominately mutually trans, which process comprises reacting a 4-aryl-1-bromo-2-fluoro-2-butene compound having the structural formula III



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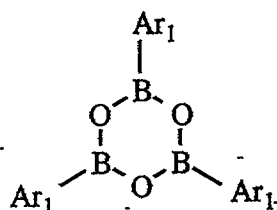


wherein Ar, R and R₁ are as described above with a palladium catalyst, and a boronic acid having the structural formula IV, a boronic anhydride having the structural formula V or a borate ester having the structural formula VI

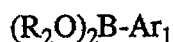


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-24-



(V)



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wherein R_2 is C_1 - C_4 alkyl and Ar_1 is as described above.

12. The process according to claim 11 wherein the palladium catalyst is selected from the group consisting of bis(dibenzylideneacetone)palladium(0), tetrakis(triphenylphosphine)palladium(0), bis(acetonitrile)palladium(II) chloride, bis(triphenylphosphine)palladium(II) chloride, [1,4-bis(diphenylphosphine)butane]palladium(II) dichloride, [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) diacetate, palladium(II) acetate, palladium(II) chloride and palladium on activated carbon and mixtures thereof; and the base is selected from the group consisting of an alkali metal carbonate, an alkaline earth metal carbonate, an alkali metal hydrogen carbonate, an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkali metal C_1 - C_6 alkoxide, thallium(I) carbonate, a thallium(I) C_1 - C_6 alkoxide, thallium(I) hydroxide and a tri(C_1 - C_4 alkyl)amine and mixtures thereof.



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-25-

13. The process according to claim 12 wherein the palladium catalyst is bis(dibenzylideneacetone)palladium(0) and the base is an alkali metal carbonate.

14. A process according to any one of claims 11 to 13, wherein the reaction is carried out at a temperature of about 50°C to 130°C in the presence of a solvent.

15. The process according to claim 14 wherein the solvent is selected from the group consisting of an aromatic hydrocarbon, a halogenated aromatic hydrocarbon, a carboxylic acid amide, a glycol, a C₁-C₄alcohol, a ketone and an ether and mixtures thereof and mixtures with water.

16. A process according to any one of claims 11 to 15, which comprises reacting the compound having formula III with about 0.001 to 0.1 molar equivalent of palladium catalyst, at least about 2 molar equivalents of the base, and the compound having formula IV, V or VI.

17. A process as claimed in any one of claims 11 to 16 wherein R, R₁, Ar and Ar₁ are as defined in claim 9.

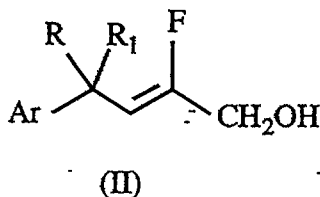
18. The process according to claim 17 wherein R, R₁, Ar and Ar₁ are as defined in claim 10.

19. A process for making a compound having formula III as illustrated in claim 1 wherein Ar, R and R₁ are as defined in claim 1, and the configuration of the groups ArCRR₁- and -CH₂Br about the double bond being predominately mutually trans; which process comprises reacting a 4-aryl-2-fluoro-2-butene-1-ol compound having structural formula II



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-26-



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wherein R, R₁ and Ar are as defined above with a brominating agent.

20. A process as claimed in claim 19 wherein the brominating agent is selected from the group consisting of a bromine-triphenyl phosphine complex, phosphorus tribromide, thionyl bromide, HBr, and mixtures thereof.

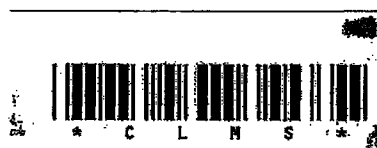
21. A process as claimed in claim 19 or 20 carried out in a solvent at a temperature of about 50-130°C.

22. A process as claimed in claim 1, carried out substantially as described herein with reference to any one of the Examples herein.

23. A process as claimed in claim 11, carried out substantially as described herein with reference to Example 2 or 4 herein.

24. A process as claimed in claim 19, carried out substantially as described with reference to Example 1 or 3 herein.

25. A compound having the formula I whenever prepared by a process as claimed in any one of claims 1 to 18, 22 and 23.



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-27-

26. A compound having the formula III, whenever prepared by a process as claimed in any one of claims 19 to 21 and 24.

27. A compound having the formula III as illustrated in claim 1 where Ar, R and R₁ are as defined in claim 1; the configuration of the groups ArCRR₁- and CH₂Br about the double bond being predominately mutually trans.

28. A compound as claimed in claim 27 wherein R, R₁ and Ar are as defined in claim 9.

29. A compound as claimed in claim 28, wherein R, R₁ and Ar are as defined in claim 10.

30. The compound according to claim 27 selected from the group consisting of
1-(p-chlorophenyl)-1-(3-bromo-2-fluoropropenyl)cyclopropane,
(Z)-; and
1-bromo-4-(p-chlorophenyl)-2-fluoro-4-methyl-2-pentene,
(Z)-.

