



597601

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952



CONVENTION APPLICATION FOR A PATENT

We, E.I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, 19398, United States of America, hereby apply for the grant of a patent for an invention entitled, "INSECTICIDAL AND ACARICIDAL PHENOXYPYRIDINYL ESTERS AND INTERMEDIATES", which is described in the accompanying complete specification.

This application is a Convention Application and is based on the application for a patent or similar protection made in the United States of America on 8 November 1985 and made in the United States of America on 26 September 1986 respectively numbered 796,152 and 910,942.

Our address for service is: Care of JAMES M. LAWRIE & CO., Patent Attorneys of 72 Willsmere Road, Kew, 3101, Victoria, Australia.

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 16.3.90
DATED this 6 day of November 1986

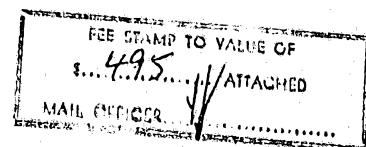
JAMES M. LAWRIE & CO.

By:

Jeffrey A. Ryker

Patent Attorneys for

E.I. DU PONT DE NEMOURS AND COMPANY



Declaration in Support of an Application for a Patent

(Combined Form - Convention ~~XXXXXX~~)

* Strike out for
non-convention

In support of the *Convention* application made for a ~~patent~~ ^{patent} ~~of addition~~ for an
invention entitled "INSECTICIDAL AND ACARICIDAL
PHENOXYPYRIDINYL ESTERS AND INTERMEDIATES"

Insert full
name and address
of declarant

I, Donald Allen Hoes, Asst. Secretary of the Patent Board of
E. I. DU PONT DE NEMOURS AND COMPANY, 2718-A Montchanin Bldg.,
Wilmington, Delaware 19898, United States of America

do solemnly and sincerely declare as follows:-

- ~~1. I am authorised by the applicant (or for the applicant) to make this declaration on its behalf.~~
~~(or in the case of an application by a body corporate)~~

1. I am authorised by E. I. DU PONT DE NEMOURS AND COMPANY
the applicant for the ~~patent~~ ^{patent} ~~of addition~~ to make this declaration on its behalf.

Strike out Para. 2.
for non-convention

2. The basic application(s) as defined by section 141 of the Act ~~was~~ ^{were} made in
the United States of America
on the 8th day of November 1985, No. 796,152
by George Philip LAHM, and
on the 26th day of September 1986, No. 910,942
by George Philip LAHM, and
on the day of 19....., No.
by

- ~~3. I am authorised by the applicant (or for the applicant) to make this declaration on its behalf.~~
~~(or in the case of an application by a body corporate)~~

Insert full
name(s) and
address(es) of
inventor(s)

3. George Philip LAHM
of 25 Winding Hill Drive
Hockessin, Delaware 19707
United States of America

is the actual inventor(s) of the invention and the facts upon which ~~the~~ ^{the}
said Corporation is entitled to make the application are as
follows:- E. I. DU PONT DE NEMOURS AND COMPANY is the assignee
of the invention and of the priority right from the said
actual inventor(s)

Strike out Para. 4
for non-convention

4. The basic application(s) referred to in paragraph 2 of this Declaration ~~was~~ ^{were} the
first application(s) made in a Convention country in respect of the invention the subject of the
application.

DECLARED AT Wilmington, Delaware, U.S.A.

this 10th

day of October

1986.

Donald Allen Hoes

(12) PATENT ABRIDGMENT (11) Document No. AU-B-64934/86
 (19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 597601

(54) Title
 PHENOXYPYRIDINYL ESTERS AND INTERMEDIATES

International Patent Classification(s)
 (5) C07D 213/64 A01N 043/40 C07D 213/65 C07D 213/68
 C07D 213/70 C07D 405/12

(21) Application No. : 64934/86 (22) Application Date : 07.11.86

(30) Priority Data

(31) Number	(32) Date	(33) Country
796152	08.11.85	US UNITED STATES OF AMERICA
910942	26.09.86	US UNITED STATES OF AMERICA

(43) Publication Date : 14.05.87

(44) Publication Date of Accepted Application : 07.06.90

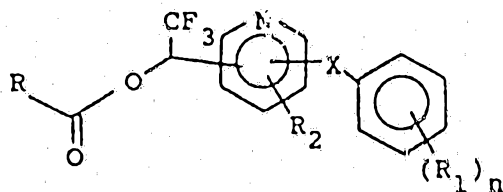
(71) Applicant(s)
 E.I. DU PONT DE NEMOURS & COMPANY

(72) Inventor(s)
 GEORGE PHILIP LAHM

(74) Attorney or Agent
 CALLINAN LAWRIE

(57) Claim

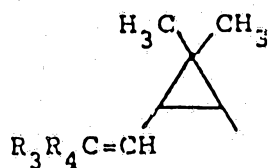
1. A phenoxy pyridinyl compound of the formula



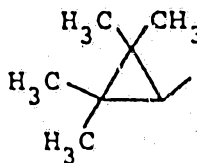
characterized by a 1,3-relationship between the ester and the ether substituents on the pyridine ring.

wherein:

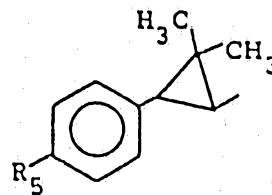
R is



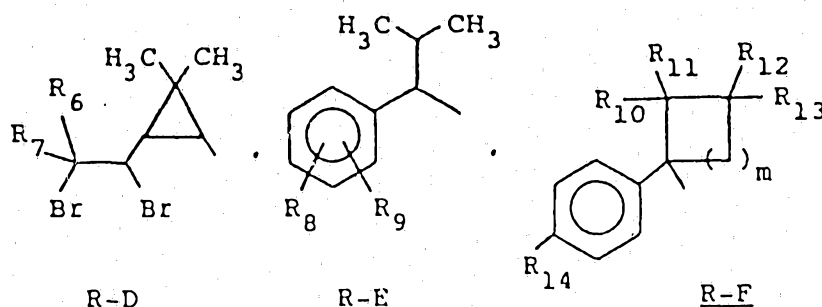
R-A



R-B



R-C



X is O or S;

n is 1 to 3;

m is 0 or 1;

R_1 is H, C_1 to C_4 alkyl, C_2 to C_5 alkenyl, C_2 to C_5 alkynyl, C_1 to C_4 haloalkyl, C_1 to C_4 alkoxy, C_1 to C_4 haloalkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkylsulfinyl, C_1 to C_4 alkylsulfonyl, C_1 to C_4 haloalkylthio, C_1 to C_4 haloalkylsulfonyl, F, Cl, Br; when $n = 2$, the R_1 substituents, taken together, can be 3,4-methylenedioxy;

R_2 is H, F, Cl, Br, CH_3 , or CF_3 ;

R_3 is F, Cl, Br, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, CO_2CH_3 , or $CO_2CH_2CH_3$;

R_4 is F, Cl, Br, or CH_3 ;

R_5 is H, F, Cl, CF_3 , or C_1 to C_4 alkyl;

R_6 is Cl or Br;

R_7 is Cl or Br;

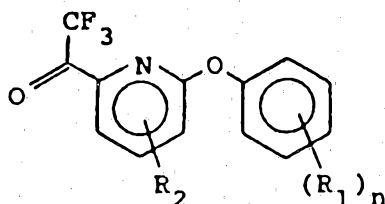
R_8 is H, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, C_1 to C_4 alkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkylsulfinyl, C_1 to C_4 alkylsulfonyl, C_1 to C_4 haloalkylthio, C_1 to C_4 haloalkylsulfinyl, C_1 to C_4 haloalkylsulfonyl, F, Cl or Br;

R_9 is H, F, Cl, CH_3 , OCH_3 , or R_8 and R_9 , taken together, can be 3,4-methylenedioxy;

R_{10} , R_{11} , R_{12} and R_{13} are independently H, F, or Cl; and

R_{14} is H, F, Cl, OCH_3 , OCH_2CH_3 , or C_1 to C_2 haloalkoxy.

7. A compound of the formula

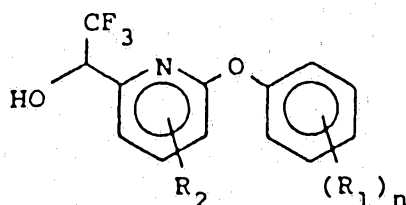


wherein:

R_1 is H, C_1 to C_4 alkyl, C_2 to C_5 alkenyl, C_2 to C_5 alkynyl, C_1 to C_4 haloalkyl, C_1 to C_4 alkoxy, C_1 to C_4 haloalkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkylsulfinyl, C_1 to C_4 alkylsulfonyl, C_1 to C_4 haloalkylthio, C_1 to C_4 haloalkylsulfonyl, F, Cl, Br; when $n = 2$, the R_1 substituents, taken together, can be 3,4-methylenedioxy;

R_2 is H, F, Cl, Br, CH_3 or CF_3 ; and
 n is 1 to 3.

8. A compound of the formula



wherein:

R_1 is H, C_1 to C_4 alkyl, C_2 to C_5 alkenyl, C_2 to C_5 alkynyl, C_1 to C_4 haloalkyl, C_1 to C_4 alkoxy, C_1 to C_4 haloalkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkylsulfinyl, C_1 to C_4 alkylsulfonyl, C_1 to C_4 haloalkylthio, C_1 to C_4 haloalkylsulfonyl, F, Cl, Br; when $n = 2$, the R_1 substituents, taken together, can be 3,4-methylenedioxy;

R_2 is H, F, Cl, Br, CH_3 , or CF_3 ; and
 n is 1 to 3.



597601

Form 10

PATENTS ACT 1952-1973

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

Class:

Int. Cl:

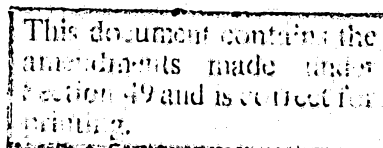
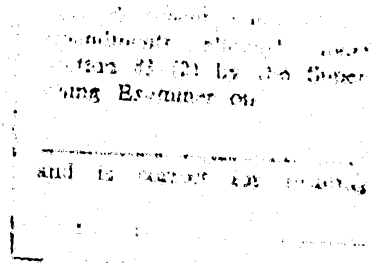
Application Number:
Lodged:

64934/86

Complete Specification—Lodged:
Accepted:
Published:

Priority:

Related Art:



TO BE COMPLETED BY APPLICANT

Name of Applicant:

E.I. DU PONT DE NEMOURS AND COMPANY, a corporation
organised and existing under the laws of the State
of Delaware, located at Wilmington, State of
Delaware, 19898, United States of America.

Address of Applicant:

Actual Inventor:

GEORGE PHILIP LAHM

Address for Service:

Care of: JAMES M. LAWRIE & CO., Patent Attorneys of
72 Willsmere Road, Kew, 3101, Victoria, Australia.

Complete Specification for the invention entitled: "INSECTICIDAL AND ACARICIDAL
PHENOXYPYRIDINYL ESTERS AND INTERMEDIATES"

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

*Note: The description is to be typed in double spacing, pica type face, in an area not exceeding 250 mm in depth and 160 mm in width, on tough white paper of good quality and it is to be inserted inside this form.

Insecticidal and Acaricidal
Phenoxypyridinyl Esters and Intermediates

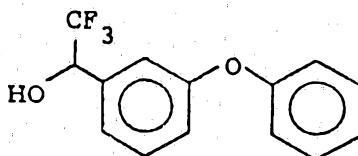
Cross Reference to Related Application

This application is a continuation-in-part of
copending application bearing U.S. Serial No. 795,152
filed on November 8, 1985.

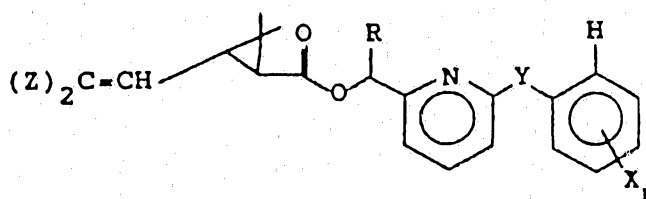
Background of the Invention

This invention concerns phenoxypyridinyl ester
insecticides and acaricides, intermediates for their
preparation, agricultural compositions containing the
insecticides and acaricides and their use to control
pests.

U.S. 4,162,366 discloses the following alcohol
for use in the preparation of insecticidal esters:



DE 2,810,881 discloses compounds of the following
formula as insecticides:



wherein

X is independently C_1 to C_4 alkyl, C_1 to C_4
alkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkyl-
sulfonyl, CF_3 , 3,4-methylenedioxy, Cl, F,
or Br;

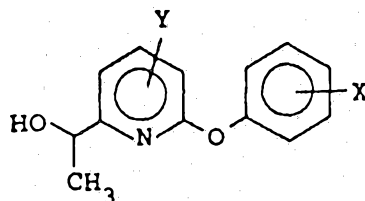
n is 0, 1 or 2;

Y is O or S;

R is H, CN, or $C\equiv CH$; and

Z is Cl, F or Br.

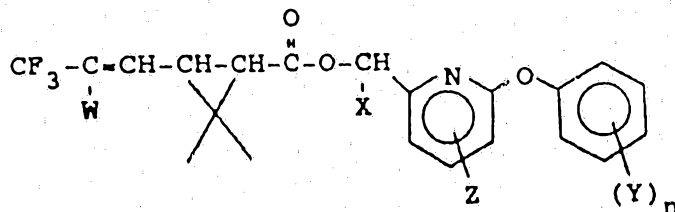
EP 145,661 discloses the following intermediates in the synthesis of insecticides:



wherein

10 X and Y are H, halo, NO_2 , C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, C_1 to C_4 alkoxy, C_2 to C_5 alkenyl, or C_2 to C_5 alkynyl.

AU 84/34,055 discloses compounds of the following formula as insecticides:



20 wherein

W is halogen;

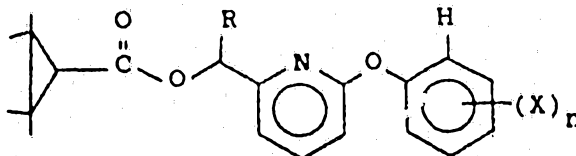
X is H, CN, or $\text{C}\equiv\text{CH}$;

25 Y is H, C_1 to C_4 alkyl, C_1 to C_4 alkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkylsulfonyl, CF_3 , 3,4-methylenedioxy, Cl, F or Br;

n is 1 or 2; and

Z is H, Cl or F.

U.S. 4,221,799 discloses compounds of the following formula as insecticides:



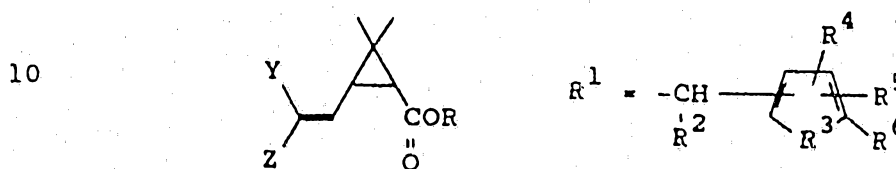
wherein

35 n is 0, 1, or 2;

X is independently C_1 to C_4 alkyl, C_1 to C_4 alkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkylsulfinyl, C_1 to C_4 alkylsulfonyl, CF_3 , NO_2 , CN, Cl, F, Br, or 3,4-methylenedioxy; and

5 R is H, CN, or $C\equiv CH$.

U.S. 4,332,815 discloses compounds of the following formula as insecticides:



wherein

15 one of Y and Z is C_1 to C_4 perhaloalkyl and the other is H, halo, lower alkyl, phenyl, phenylthio, or benzyl;

provided that Y and Z may be combined to form a perhalocyclopentylidene group;

20 R is allethrolonyl, tetrahydropthalimidomethyl, or R^1 ;

provided that R^1 is other than phenoxybenzyl, α -cyanophenoxybenzyl, or α -ethynylphenoxybenzyl;

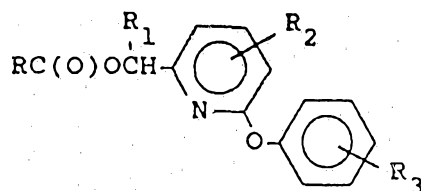
25 R^2 is H, lower alkyl, ethynyl, CN, or trihalomethyl;

R^3 is divalent O, divalent S, or vinylene; and

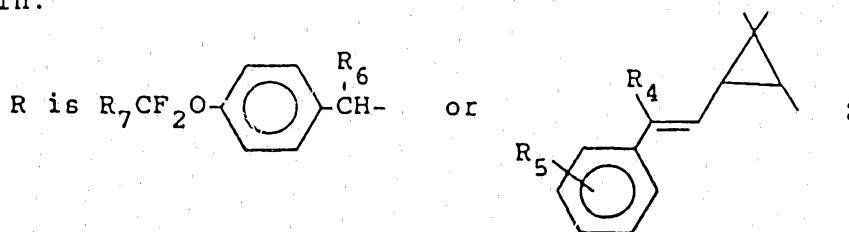
30 R^4 , R^5 , and R^6 are independently H, lower alkyl, halogen, lower alkenyl, phenyl, phenoxy, benzyl, phenylthio, or any two joined to form a divalent methylenedioxy group;

provided that when R^4 , R^5 or R^6 contains a phenyl ring, it may be substituted with one to three substituents selected from halogen or lower alkyl.

European Patent Application 61,114 discloses esters of the following formula to be useful as insecticides:



wherein:



15 R_1 is H, CN or optionally halo substituted C_1-C_4 alkyl, alkenyl or alkynyl;

R_2 is H or halogen;

R_3 is H or halogen;

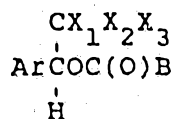
20 R_4 is H, Cl, Br, CN or optionally halo substituted alkyl;

R_5 is H, halogen or optionally halo substituted alkyl or alkoxy;

R_6 is isopropyl or cyclopropyl; and

25 R_7 is H, F, CF_3 , $CHFC1$ or CF_2Cl .

G.B. 2,108,123 discloses esters of the following formula to be useful as insecticides:

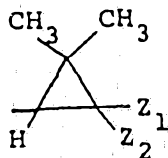


wherein:

Ar represents an optionally substituted aromatic or heteroaromatic radical;

35 X_1 , X_2 , and X_3 , which may be the same or different each represent a hydrogen atom or a halo-

gen atom, with the proviso that at least one represents a halogen atom; and B represents an alkyl radical of from 1 to 18 carbon atoms or a radical of the formula

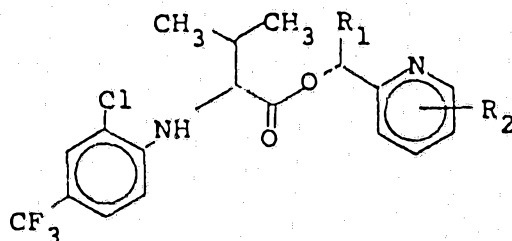


10

with the exception of compounds of the general formula in which X_1 , X_2 and X_3 each represents a fluorine.

Recent Advances In The Chemistry Of Insect Control, Janes (ed.), Royal Society of Chemistry, Burlington House, 1985, page 153, discloses a table of phenoxypyridyl esters of the formula:

20

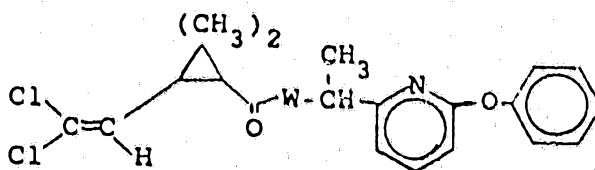


wherein:

R_1 is H, CN, CH_3 , CH_2CH_3 , ethynyl, ethenyl, CF_3 or CH_3CO_2 and R_2 is phenyl or phenoxy.

U.S. 4,323,574 discloses compounds of the following formula as insecticides

30



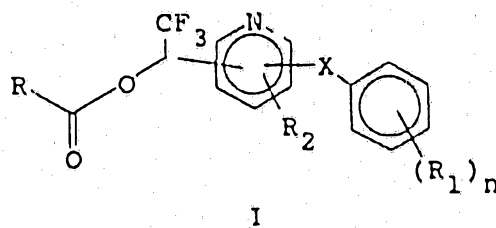
wherein:

35

W is O or S.

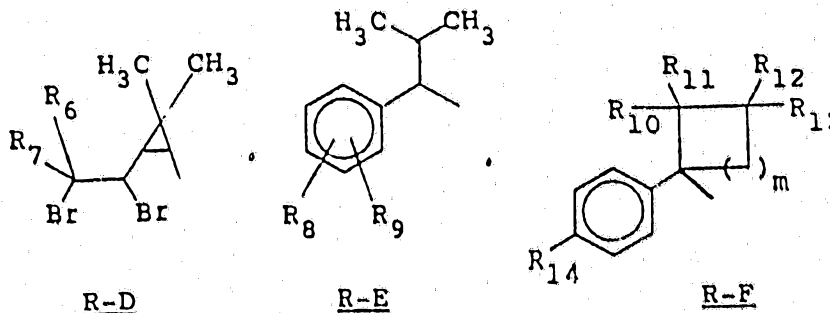
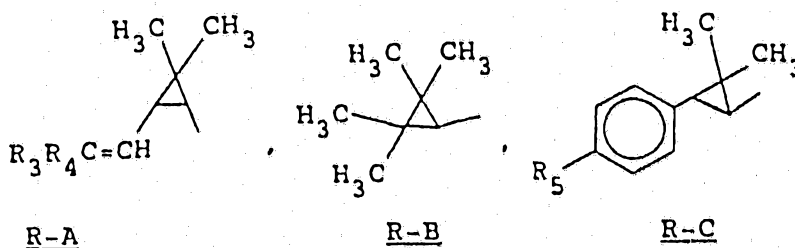
Summary of the Invention

This invention concerns phenoxy pyridinyl ester compounds of Formula I, suitable agricultural compositions containing them, and use of said compounds as insecticides. Compounds of Formula I are characterized by a 1,3 relationship between the ester ($\text{RCO}_2\text{CHCF}_3$ -) and ether (-x- optionally substituted phenyl) substituents on the pyridine ring. This invention includes all geometric and stereoisomer forms of such compounds of Formula I. This invention also concerns particular alcohol and ketone intermediates employed to make the compounds of Formula I and processes for making said intermediates. The intermediates are likewise characterized by a 1,3 relationship between the alcohol/ketone and ether substituents on the pyridine ring.



wherein:

R is



X is O or S;

n is 1 to 3;

m is 0 or 1;

5 R_1 is H, C_1 to C_4 alkyl, C_2 to C_5 alkenyl, C_2 to C_5 alkynyl, C_1 to C_4 haloalkyl, C_1 to C_4 alkoxy, C_1 to C_4 haloalkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkylsulfinyl, C_1 to C_4 alkylsulfonyl, C_1 to C_4 haloalkylthio, C_1 to C_4 haloalkylsulfonyl, F, Cl, Br; when n = 2, the
10 R_1 substituents, taken together, can be 3,4-methylenedioxy;

R_2 is H, F, Cl, Br, CH_3 , or CF_3 ;

R_3 is F, Cl, Br, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, CO_2CH_3 , or $CO_2CH_2CH_3$;

15 R_4 is F, Cl, Br, or CH_3 ;

R_5 is H, F, Cl, CF_3 , or C_1 to C_4 alkyl;

R_6 is Cl or Br;

R_7 is Cl or Br;

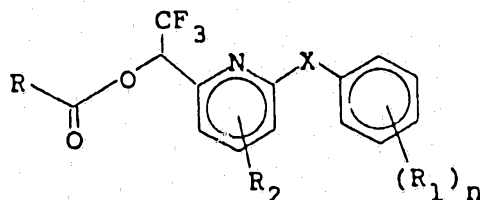
20 R_8 is H, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, C_1 to C_4 alkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkylsulfinyl, C_1 to C_4 alkylsulfonyl, C_1 to C_4 haloalkylthio, C_1 to C_4 haloalkylsulfinyl, C_1 to C_4 haloalkylsulfonyl, F, Cl or Br;

25 R_9 is H, F, Cl, CH_3 , OCH_3 , or R_8 and R_9 , taken together, can be 3,4-methylenedioxy;

R_{10} , R_{11} , R_{12} and R_{13} are independently H, F, or Cl; and

30 R_{14} is H, F, Cl, OCH_3 , OCH_2CH_3 , or C_1 to C_2 haloalkoxy.

Preferred compounds are those of Formula Ia wherein the substituent values are as previously defined:



Ia

More preferred compounds are those of Formula Ia wherein:

X is O;

n is 1;

m is 1;

R_1 is H, CH_3 , CF_3 , OCH_3 , OCF_2H , F, Cl, SCH_3 , SO_2CH_3 , SCF_2H , or SO_2CF_2H ;

R_2 is H, F, or Cl;

R_3 is H, F, Cl, or C_1 to C_2 alkoxy;

R_9 is H; and

R_{14} is H, F, Cl, OCH_3 , OCH_2CH_3 or OCF_2H .

Most preferred compounds are those of Formula Ia wherein R is selected from R-A, R-B, R-D and R-E, the remaining substituents being as defined above with respect to "more preferred" compounds.

Preferred species wherein R is R-A are as follows:

- [1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate;
- [1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate;
- [1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate;

- [1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl]
cis-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate;
- [1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl]
5 (1R)-cis-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate;
- [1-(6-Phenoxy-2-pyridinyl)-(S)-2,2,2-trifluoroethyl]-(1R)-cis-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate;
- 10 • [1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl]
cis-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate;
- [1-(6-Phenoxy-2-pyridinyl)-(R)-2,2,2-trifluoroethyl]-(1S)-cis-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate
15 plus [1-[6-phenoxy-2-pyridinyl]-(S)-2,2,2-trifluoroethyl]-(1R)-cis-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate;
- [1-(6-Phenoxy-2-pyridinyl)-(S)-2,2,2-trifluoroethyl]-(1R)-cis-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate;
20
- [1-[6-(4-Fluorophenoxy)-2-pyridinyl]-2,2,2-trifluoroethyl]-cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate; and
- 25 • [1-[6-(4-Fluorophenoxy)-2-pyridinyl]-(R)-2,2,2-trifluoroethyl]-(1S)-cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate plus [1-[6-(4-fluorophenoxy)-2-pyridinyl]-(S)-2,2,2-trifluoroethyl]-(1R)-cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate.
30

Preferred species wherein R is R-B are as follows:

- [1-[6-Phenoxy-2-pyridinyl]-2,2,2-trifluoroethyl]
2,2,3,3-tetramethylcyclopropanecarboxylate; and

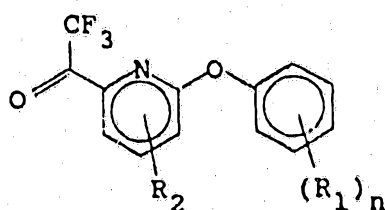
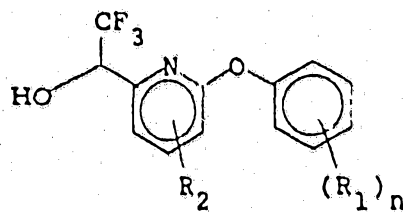
- [1-[6-(4-Fluorophenoxy)-2-pyridinyl]-2,2,2-trifluoroethyl]-2,2,3,3-tetramethylcyclopropanecarboxylate.

A preferred species wherein R is R-D is [1-[6-phenoxy-2-pyridinyl]-2,2,2-trifluoroethyl]-(1R)-cis-2,2-dimethyl-3-(1,2,2,2-tetrabromoethyl)-cyclopropanecarboxylate.

A preferred species wherein R is R-E is [1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 4-chloro- α -(1-methylethyl)benzene acetate.

The optical isomer designations of the preferred species are based on analogy to other pyrethroids. Preparation of said compounds will be described hereafter.

Intermediates of this invention are compounds of Formula II and Formula III:

IIIII

wherein R_1 , R_2 , and n are as defined previously.

Preferred intermediates are those employed to make the corresponding preferred insecticidal and acaricidal compounds, including:

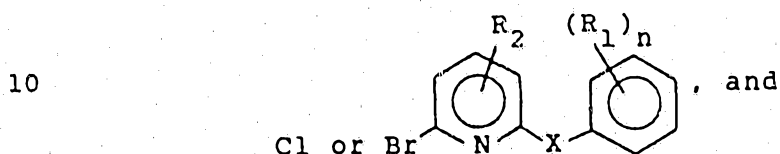
- 1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethanol;
- 1-(6-Phenoxy-2-pyridinyl)-(S)-2,2,2-trifluoroethanol; and
- 1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethanol.

The agricultural compositions of this invention and the method for using them to control pests will be

described in more detail in the Utility, Formulation and Application Sections of this disclosure.

The process of this invention concerned with making the novel ketone intermediates comprises the 5 steps, in sequence, of:

- (i) metallating the following phenoxy or thiophenoxy pyridinyl halide,



- (ii) reacting the metallated product of step (i) with N,N-dimethyltrifluoroacetamide ($\text{CF}_3\text{CON}(\text{CH}_3)_2$) to 15 form the corresponding phoxypyridinyltrifluoroethanone wherein: R_1 , R_2 , X and n are as previously defined.

- The described alcohol intermediates are made by 20 (iii) reducing the ketone of step (ii), preferably with a hydride reducing agent, most preferably with NaBH_4 .

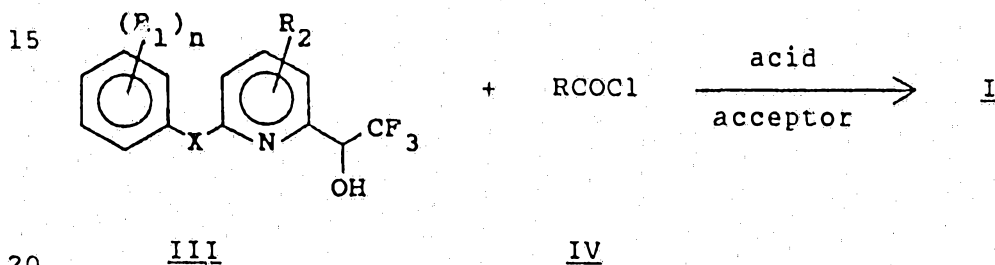
25

30

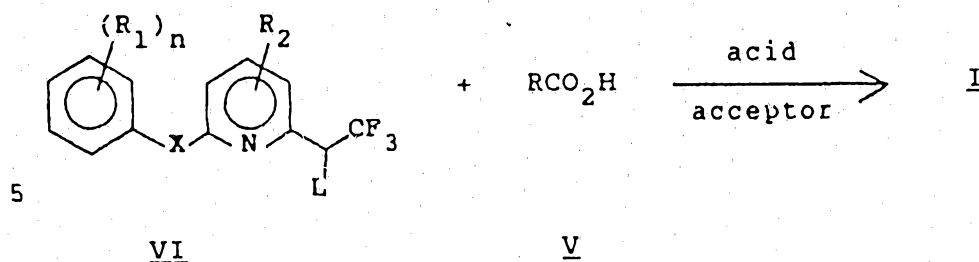
35

Details of the Invention

Compounds of Formula I can be prepared by the reaction of pyridine alcohols of Formula III with any of the conventional pyrethroid acid chlorides of Formula IV. Typical reactions involve the combination of equimolar amounts of III and IV in the presence of an amine base such as triethylamine or pyridine at temperatures generally in the range of 0° to 40°C. Suitable solvents include ether, tetrahydrofuran, chloroform and benzene. For clarity, only the 2,6-isomer of III is depicted; however, it is understood that the procedures that follow apply to each of the pyridine isomers disclosed.



An alternate approach to compounds of Formula I, which may be preferred where the intermediate acid chloride of Formula IV is of low stability, is the reaction of a pyrethroid acid of Formula V with a pyridine of Formula VI, wherein L represents a suitable leaving group such as Cl, Br, methanesulfonyloxy and p-tolylsulfonyloxy. For example, equimolar amounts of V and VI can be combined in the presence of an alkali metal carbonate or alkali metal bicarbonate in a polar aprotic solvent such as dimethylformamide or dimethylsulfoxide to afford the esters of Formula I. The reaction can be conducted at temperatures ranging from about 0° to 80°C, although temperatures in the range of 20° to 60°C are preferred.



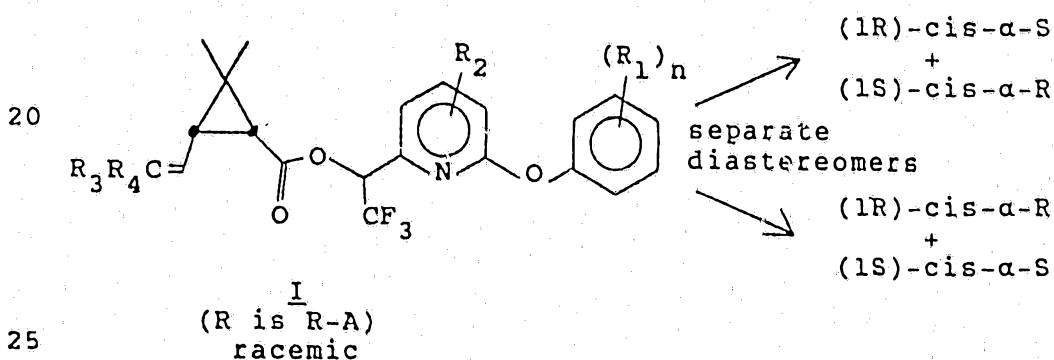
An alternate approach to compounds of Formula I is the reaction of an alcohol of Formula III with an acid of Formula V in the presence of a dehydrating agent such as dicyclohexylcarbodiimide (DCC). The reaction is conducted in a solvent such as ether or methylene chloride and generally in the presence of an amine base such as pyridine.

15 It is to be recognized that compounds of Formula I include a number of both geometrical and optical isomers which may differ dramatically in biological activity. In some instances, it may be desirable to obtain compounds which are geometrically and/or optically pure or which are enriched in one or more of the possible isomers.

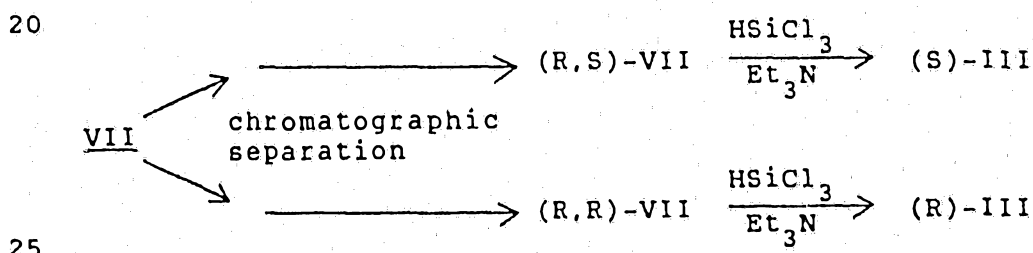
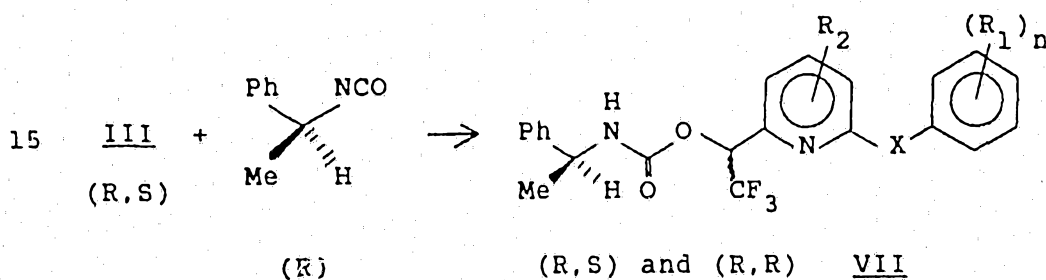
20 It is well recognized that compounds of the pyrethroid class require a specific spatial orientation for optimum levels of activity. Generally, a single enantiomer is responsible for most of the observed activity (see, e.g., "Recent Advances in the Chemistry of Insect Control", ed. Janes, Royal Society of Chemistry, Burlington House, 1985, p. 26). Based on the known spatial requirements, compounds of the present invention would be predicted to exhibit their highest levels of activity for compounds derived from the S-alcohol of Formula III. The absolute configuration of the more active isomer of the acid portion (V) is dependent on the specific acid used (where R is R-A through R-F). However, for each of

the acid groups the same spatial orientation is required for optimum activity.

As an example, an isomer mixture of Formula I derived from a racemic alcohol of Formula III and a racemic acid of Formula V (where R is R-A with a cis cyclopropane) consists of a mixture of racemic diastereomers. The diastereomeric mixture can be separated by either fractional recrystallization or chromatography. The enantiomeric pair containing the (1R)-cis- α -S enantiomer is expected to show the greater level of activity (note that in the designation (1R)-cis- α -S that (1R)-cis refers to a cis cyclopropane wherein carbon number 1 is of the R configuration, and α -S refers to the asymmetric center α to the pyridine ring and possessing the S configuration).



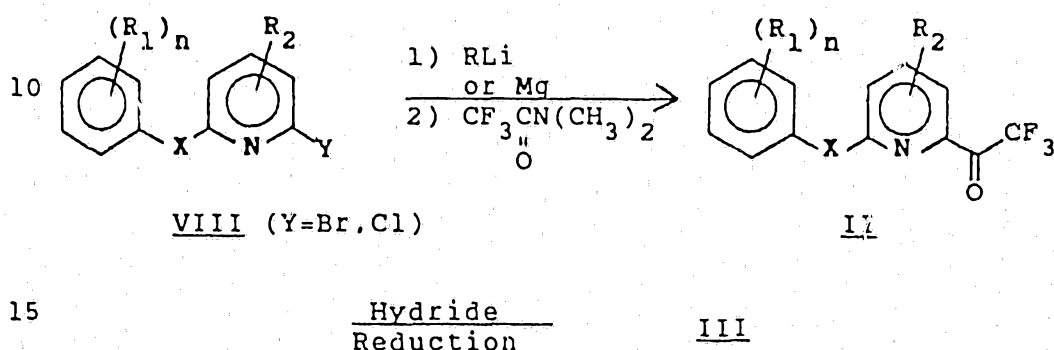
Resolution of the alcohol of Formula III can be accomplished by any of a number of suitable methods known in the art for the resolution of alcohols in general. One such method involves reaction of racemic
 5 III with an optically active resolving agent, such as (R)-(+)-1-phenylethyl isocyanate, chromatographic separation of the diastereomeric carbamates VII and, finally, regeneration of the resolved alcohol. Other suitable resolving agents include R-(-)-1-(1-naphthyl)-
 10 ethyl isocyanate and (R)-(+)- α -methoxy- α -(trifluoromethyl)phenylacetic acid.



Novel intermediates of Formula VI can be prepared from the alcohols of Formula III by any of the known methods for conversion of a hydroxy group to a suitable leaving group. For example, the methanesulfonates of
 30 Formula VI (L is OSO_2CH_3) can be prepared by the reaction of methanesulfonyl chloride with compounds of Formula III in the presence of an amine base such as triethylamine. Chlorides of Formula VI (where L is Cl) can be prepared by reaction of III with, for
 35

example, thionyl chloride. Variants of these reactions are well documented in the chemical literature and would be known to one skilled in the art.

Pyridines of Formula III are available in two steps from halopyridines VIII via (a) introduction of the trifluoroacetyl group to form II and (b) hydride reduction of II to the alcohol III:

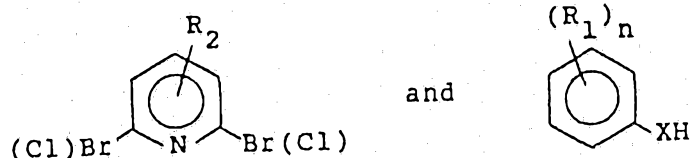


Reaction of VIII (Y=Br) with an alkyl lithium, such as *n*-butyllithium, to effect metal-halogen exchange, at temperatures ranging from 0° to -100°C and in a solvent such as tetrahydrofuran or ether, followed by reaction of the preformed pyridinyl lithium salt with N,N-dimethyltrifluoroacetamide or an alkali metal salt of trifluoroacetic acid affords the novel trifluoroacetylpyridines of Formula II.

Alternatively, treatment of VIII with magnesium to effect Grignard formation, at temperatures ranging from 60° to -80°C and in solvents such as tetrahydrofuran or ether, followed by reaction with N,N-dimethyltrifluoroacetamide affords the trifluoroacetylpyridines of Formula II. These in turn are readily reduced to the alcohols of Formula III by any of a number of the standard methods, examples of which include the hydride reducing agents lithium aluminum hydride and sodium borohydride.

The intermediate halopyridines (VIII) can be prepared from 2,6-dihalopyridines and an optionally substituted phenol or thiophenol. As an example, reaction of equimolar quantities of

5



10 in a solvent such as acetone, methyl ethyl ketone, acetonitrile, tetrahydrofuran or dimethylformamide in the presence of a base such as potassium carbonate or sodium hydride affords the 2-halopyridinyl ethers of Formula VIII.

15 Compounds of Formula IV and V are well known in the chemical literature. Those skilled in the art will recognize these to be, or to be derived from, the acid component of the synthetic pyrethroid insecticides. Selected references to these are as follows: For com-
 20 pounds where R is R-A see South African Patent Application 73/3528, U.S. 4,332,815 and U.S. 4,157,397; where R is R-B see Ger. Offen. Pat. 2,407,024 and U.S. 4,221,799; where R is R-C see Jap. Pat. Appl. J5 7,040,463; where R is R-D see Ger. Pats. 2,742,546
 25 and 2,742,547; where R is R-E see U.S. 4,062,968; and where R is R-F see European Pat. Appl. 002620 and U.S. 4,360,690.

The following Examples illustrate the invention.

30

35

Example 1Step A. 2-Bromo-6-phenoxy pyridine

To a solution of 6.5 g (0.135 mol) of 50% sodium hydride in 75 ml of dimethylformamide at 0°C and under N₂ was added a solution of 11.9 g (0.127 mol) of phenol in 75 ml of dimethylformamide. Once dropwise addition was complete, 30.0 g (0.127 mol) of 2,6-dibromopyridine was added in one portion and the mixture was heated at 60° to 65°C for 18 hours. The mixture was then cooled and partitioned between ether and 1N aqueous NaOH. The ether extracts were washed two times with aqueous NaHCO₃, dried over MgSO₄, filtered and concentrated under vacuum. The solid residue was slurried in hexane, filtered and dried to afford 25.1 g (79%) of the title compound as a white powder: m.p. 83° to 86°C; ¹H NMR (CDCl₃) δ 6.70 (d, 1H), 7.0-7.5 (m, 7H).

Step B. 2,2,2-Trifluoro-1-(6-phenoxy-2-pyridinyl)-ethanone

A solution of 12.5 g (0.05 mol) of the 2-bromo-6-phenoxy pyridine of Step A in 100 ml of dry tetrahydrofuran was cooled under N₂ to -70°C. To this solution was added 20 ml (0.052 mol) of 2.6M *n*-butyllithium in hexane at such a rate that the reaction temperature was maintained below -60°C. The reaction was stirred 5 minutes and then 7.75 g (0.055 mol) of N,N-dimethyltrifluoroacetamide in 15 ml of tetrahydrofuran was added at such a rate that the reaction was maintained below -60°C. Once addition was complete, the -70°C bath was removed and the reaction was stirred for one hour with gradual warming. After this time, 50 ml of 5% aqueous NaHCO₃ were added and the tetrahydrofuran was removed under vacuum. The aqueous residue was extracted twice with chloroform, and the

chloroform extracts were then dried over MgSO_4 , filtered and concentrated to yield 13.6 g of an orange oil. Chromatography on silica gel afforded 7.71 g (57%) of the title compound as a yellow oil: ^1H NMR and IR suggest the title compound exists in the form of a hydrate: ^1H NMR δ 4.84 (s), 7.0-8.0 (m); IR (neat) 1588, 1735, 3400 cm^{-1} .

10 Step C. 6-Phenoxy- α -(trifluoromethyl)-2-pyridine-methanol

To a solution of 10.0 g (0.0375 mol) of the 2,2,2-trifluoro-1-(6-phenoxy-2-pyridinyl)ethanone of Step B in 100 ml of ethanol at 0°C was added 1.5 g (0.0395 mol) of sodium borohydride portionwise over 15 5 to 10 minutes. The reaction was then warmed to room temperature and stirred overnight. After this time, the reaction was quenched with 1N aqueous HCl, neutralized with aqueous NaHCO_3 and extracted with chloroform. The chloroform extracts were dried over MgSO_4 , filtered and concentrated to afford a yellow 20 oil which solidified on standing to a waxy solid. Recrystallization from 4:1 hexane-ether afforded 6.13 g (60%) of the title compound as a white powder: m.p. 75° to 77°C ; ^1H NMR (CDCl_3) δ 4.67 (d, 1H), 4.92 (dq, 1H), 6.9-7.5 (m, 7H), 7.78 (t, 1H); IR 25 (Nujol) 1570, 1600, 3390 cm^{-1} .

30 Step D. cis-[1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate

To a solution of 2.04 g (7.6 mmol) of the 6-phenoxy- α -(trifluoromethyl)-2-pyridinemethanol of Step C and 1.72 g (7.6 mmol) of cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarbonyl chloride in 30 ml of dry tetrahydrofuran was added 2.0 ml (14.2 35 mmol) of triethylamine. The reaction was stirred for

72 hours. The precipitated triethylamine hydrochloride was then filtered off and the filtrate was concentrated under vacuum. The residue was chromatographed through silica gel and then distilled bulb to bulb (bp 155°C, 0.2 mm) to afford 2.61 g (74%) of the title compound as a clear, colorless oil, which was obtained as a mixture of diastereomers as indicated by the ^1H NMR spectrum: ^1H NMR (CDCl_3) δ 1.14, 1.24, 1.26, 1.29 (4 x s, 6H), 2.0-2.2 (m, 2H), 6.0-6.2 (m, 2H), 6.90 (d, 1H), 7.1-7.5 (m, 6H), 7.75 (t, 1H); IR (neat) 1742 cm^{-1} .

Example 2

[1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 4-chloro- α -(1-methylethyl)benzeneacetate

Application of the procedure of Example 1 afforded 0.20 g (51%) of the title compound as a clear colorless oil. The ^1H NMR spectrum indicated the title compound was obtained as a mixture of diastereomers: ^1H NMR (CDCl_3) δ 0.73 (d, 3H), 1.03 (2 x d, 3H), 2.3 (m, 1H), 3.30 (2 x d, 1H), 6.05 (quintet, 1H), 6.8 (2 x d, 1H), 7.0-7.7 (m, 7H); IR (neat) 1750 cm^{-1} .

Example 3

[1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate

Application of the procedure of Example 1 afforded 0.32 g (72%) of the title compound as a clear colorless oil. The ^1H NMR spectrum indicated the product was obtained as an isomeric mixture: ^1H NMR δ 1.1-1.3 (m, 6H), 1.9-2.5 (m, 2H), 6.0-6.2 (m, 2H), 6.89 (d, 1H), 7.1-7.5 (m, 6H), 7.74 (t, 1H); IR (neat) 1750 cm^{-1} .

Example 4

cis-[(1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate

Application of the procedure of Example 1 (Step
 5 D) with 0.79 g of cis-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropane carbonyl chloride afforded 1.0 g of the title compound as a clear, colorless oil. The ^1H NMR indicated the compound was obtained as a 1:1 mixture of diastereomers. ^1H NMR
 10 (CDCl_3) δ 1.17, 1.27, 1.31, 1.34 (4 x s, 6H), 2.1 (m, 2H), 6.05, 6.10 (2 x q, 1H), 6.78, 6.82 (2 x d, 1H), 6.87 (d, 1H), 7.1-7.9 (m, 7H). IR (neat) 1748 cm^{-1} .

15

Example 5

Separation of the Diastereomeric Pairs of cis-1-[(6-phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate

Chromatographic separation (silica gel, 2% ethyl
 20 acetate/hexane) of 8.4 g of a diastereomeric mixture of Example 4 afforded 2.71 g of diastereomer A (R_f 0.45, 5% ethyl acetate/hexane), m.p. 100° to 101°C, and 2.71 g of diastereomer B (R_f 0.37, 5% ethyl acetate/hexane), m.p. 66° to 68°C. The higher R_f
 25 diastereomer (A) is designated as the (1R)-cis- α -R/(1S)-cis- α -S enantiomeric pair and the lower R_f diastereomer (B) is designated as the (1R)-cis- α -S/(1S)-cis- α -R enantiomeric pair.

Diastereomer A: ^1H NMR (CDCl_3) δ 1.26 (s, 3H), 1.34 (s, 3H), 2.13 (d, 1H), 2.25 (t, 1H), 6.05 (q, 1H), 6.75 (d, 1H), 6.86 (d, 1H), 7.1-7.5 (m, 6H), 7.75 (t, 1H). IR (Nujol®) 1738 cm^{-1} .

Diastereomer B: ^1H NMR (CDCl_3) δ 1.17 (s, 3H), 1.31 (s, 3H), 2.15 (d, 1H), 2.28 (t, 1H), 6.02 (q, 1H), 7.01 (d, 1H), 7.10 (d, 1H), 7.2 (m, 4H), 7.40 (t, 1H), 7.74 (t, 1H). IR (neat) 1735 cm^{-1} .

Assignment of configuration for diastereomer B as the (1R)-cis- α -S/(1S)-cis- α -R enantiomeric pair was based on the observation that this diastereomer was considerably more active in the biological tests. In the Examples that follow, the diastereomers possessing the highest levels of activity were designated to contain the (1R)-cis- α -S enantiomer and its optical isomer.

10 Example 6

trans-1-[(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropane carboxylate

Application of the procedure of Example 1 (Step D) with 4.22 g of trans-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarbonyl chloride afforded a 1:1 diastereomeric mixture of the title compound, the components of which were separated by chromatography (silica gel, 2% ethyl acetate/hexane) and distilled bulb to bulb to afford 2.96 g of diastereomer A (R_f 0.45, 5% ethyl acetate/hexane) and 2.92 g of diastereomer B (R_f 0.39, 5% ethyl acetate/hexane).

Diastereomer A: ^1H NMR (CDCl_3) δ 1.28 (s, 3H), 1.32 (s, 3H), 1.92 (d, 1H), 2.4 (m, 1H), 6.1 (m, 2H), 6.85 (d, 1H), 7.1-7.5 (m, 6H), 7.75 (t, 1H). IR (neat) 1638 cm^{-1} .

Diastereomer B: ^1H NMR (CDCl_3) δ 1.23 (s, 3H), 1.25 (s, 3H), 1.94 (d, 1H), 2.44 (m, 1H), 6.06 (q, 1H), 6.17 (d, 1H), 6.88 (d, 1H), 7.1-7.5 (m, 6H), 7.74 (t, 1H). IR (neat) 1636 cm^{-1} .

Example 7

Step A. [R-(R*,R*)]- and [S-(R*,S*)]-[1-(6-phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl]-1-phenylethylcarbamate

5 A stirred solution of 2.40 g (8.91 mmol) of α -trifluoromethyl-6-phenoxy-2-pyridinemethanol, 1.38 g (9.36 mmol) of (R)-(+)-1-phenylethyl isocyanate, and 22 mg (0.18 mmol) of 4-dimethylaminopyridine in 9 ml of benzene under a nitrogen atmosphere was heated at 50°C for 17 hours. The
10 reaction mixture was then diluted with 150 ml of ether and washed with 25 ml of 1N aqueous HCl, 25 ml of saturated aqueous NaHCO₃, and 25 ml of saturated aqueous NaCl. The organic layer was dried (MgSO₄) and concentrated under reduced pressure. Repeated
15 chromatography of the residue on silica gel with benzene afforded first 1.77 g (48%) of the [R-(R*,R*)] diastereomer: $R_f = 0.10$ (SiO₂, benzene); ¹H NMR (CDCl₃) δ 1.52 (d, 6.8 Hz, 3H), 4.83 (quintet, 7.1 Hz, 1H), 6.01 (q, 6.1 Hz, 1H), 6.83 (d, 8.2 Hz, 1H),
20 7.11-7.37 (br m, 12H), and 7.68 (t, 7.8 Hz, 1H); and then 1.77 g (48%) of the [S-(R*,S*)] diastereomer: $R_f = 0.09$ (SiO₂, benzene); ¹H NMR (CDCl₃) δ 1.47 (d, 6.8 Hz, 3H), 4.80 (quintet, 7.0 Hz, 1H), 5.98 (q, 6.9 Hz, 1H), 6.86 (d, 8.3 Hz, 1H), 7.13-7.42 (br m, 12H),
25 and 7.72 (t, 7.8 Hz, 1H).

Step B. (S)-(+)-6-Phenoxy- α -trifluoromethyl-2-pyridinemethanol

30 A stirred solution of 1.28 g (3.08 mmol) of the [S-(R*,S*)] carbamate from Step A, 0.52 ml (380 mg, 3.7 mmol) of triethylamine, and 0.34 ml (460 mg, 3.4 mmol) of trichlorosilane in 12 ml of toluene under a nitrogen atmosphere was heated at 60°C for 2 hours. The reaction mixture was then diluted with 50 ml of
35 saturated aqueous NH₄Cl and extracted with ether

(3 x 25 ml). After being dried (MgSO_4), the combined organic extracts were concentrated under reduced pressure and chromatography of the residue on 20 g of silica gel with 1:15 ethyl acetate/hexane afforded 667 mg (81%) of the title compound as a white solid melting at 51.5-53.5°C: $[\alpha]_D^{22} = +2.0^\circ$ (CHCl_3 , c 1.00) and $[\alpha]_{365}^{22} = +4.8^\circ$ (CHCl_3 , c 1.00). The spectral and chromatographic properties of this material were identical to those of racemic material prepared in Example 1 (Step C).

Step C. (S)-[1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] (1R)-cis-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (Enantiomer B)

To a stirred solution of 612 mg (2.52 mmol) of cis-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid, 647 mg (2.40 mmol) of the (S)-(-)-6-phenoxy- α -trifluoromethyl-2-pyridinemethanol from Step B, and 37 mg (0.30 mmol) of 4-dimethylaminopyridine in 6.0 ml of CH_2Cl_2 cooled to 0°C under a nitrogen atmosphere was added 620 mg (3.00 mmol) of 1,3-dicyclohexylcarbodiimide. After 2 hours at 0°C, the reaction mixture was diluted with 50 ml of hexane and filtered. The filtrate was concentrated under reduced pressure and chromatography of the residue on 100 g of silica gel with 1:60 ether/hexane afforded first 608 mg (51%) of Enantiomer A, assigned the (1S)-cis- α -S configuration, as a colorless oil: $[\alpha]_D^{22} = -14.5^\circ$ (CHCl_3 , c 1.20) and $[\alpha]_{365}^{22} = -104.7^\circ$ (CHCl_3 , c 1.20).

Further elution afforded 573 mg (48%) of Enantiomer B, assigned the (1R)-cis- α -S configuration, as a colorless oil: $[\alpha]_D^{22} = +48.4^\circ$ (CHCl_3 , c 1.08) and $[\alpha]_{365}^{22} = +183.8^\circ$ (CHCl_3 , c 1.08). The spectral and chromatographic properties of this material were identical to those of racemic material prepared in Example 5.

Example 8

[1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl]
trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-
carboxylate

Application of the procedure of Example 1 (Step
 5 D) with 1.9 g of trans-3-(2,2-dichloroethenyl)-2,2-
dimethylcyclopropane carbonyl chloride afforded 1.78 g
 (48%) of the title compound as a viscous yellow oil.
 The ^1H NMR indicated the product to consist of a 1:1
 mixture of diastereomers. ^1H NMR (CDCl_3) δ
 10 1.20, 1.21, 1.24, 1.28 (4 x s, 6H), 1.8 (m, 1H), 2.3
 (m, 1H), 5.64, 5.66 (2 x d, 1H), 6.1 (m, 1H), 6.88 (d,
 1H), 7.1-7.8 (m, 7H). IR (neat) 1750 cm^{-1} .

Example 9

15 [1-[6-(4-Fluorophenoxy)-2-pyridinyl]-2,2,2-trifluoro-
 ethyl]-cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclo-
propane carboxylate

A solution of 12 g of 6-(4-fluorophenoxy)- α -
 trifluoromethyl-2-pyridine, ethanol and 9.7 g of
 20 cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane
carbonyl chloride in 100 ml of dry THF under an atmos-
 phere of nitrogen was cooled to 10° to 15°C and treated
 with 6.5 ml of triethylamine, added in a dropwise
 manner. The reaction mixture was stirred at room
 25 temperature for approximately 14 hours and was then
 filtered. The filtrate was concentrated under vacuum
 to afford 20.5 g of a light orange semisolid, which
 was shown by TLC analysis (silica gel; 10% ethyl
 acetate/hexanes) to consist of two components.
 30 Purification by flash chromatography gave the title
 compound as a mixture of diastereomers, m.p. $69-72^\circ\text{C}$;
 NMR (200 MHz, CDCl_3): δ 1.14 (1.2H, s), 1.24
 (1.8H, s), 1.27 (1.2H, s), 1.30 (1.8H, s), 2.0-2.2
 (2H, m), 5.95-6.2 (2H, m), 6.89 (1H, d, $J=8\text{ Hz}$),
 35 7.05-7.2 (5H, m), 7.75 (1H, t, $J=8\text{ Hz}$).

Example 10

Separation of the diastereomers of [1-[6-(4-Fluorophenoxy)-2-pyridinyl]-2,2,2-trifluoroethyl]-cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate

A 2-gram sample of the above was subjected to chromatographic purification. Elution with 5% ethyl acetate/hexanes gave 800 mg of the higher R_f diastereomer (A) (R_f 0.57, 10% ethyl acetate/hexane) as a white solid, m.p. 97° to 99°C; NMR (200 MHz, $CDCl_3$): δ 1.24 (3H, s), 1.30 (3H, s), 2.01 (1H, d, $J=8$ Hz), 2.12 (1H, t, $J=8$ Hz), 6.05 (1H, q, $J=7$ Hz), 6.09 (1H, d, $J=8$ Hz), 6.89 (1H, d, $J=8$ Hz), 7.05-7.2 (5H, m), 7.75 (1H, t, $J=8$ Hz); the lower R_f diastereomer (B) (R_f 0.50, 10% ethyl acetate/hexane) was obtained as a white solid (700 mg), m.p. 78.5-81°C; NMR (200 MHz, $CDCl_3$): δ 1.14 (3H, s), 1.27 (3H, s), 2.01 (1H, d, $J=8$ Hz), 2.14 (1H, t, $J=8$ Hz), 6.0 (1H, q, $J=7$ Hz), 6.15 (1H, d, $J=8$ Hz), 6.89 (1H, d, $J=8$ Hz), 7.05-7.2 (5H, m), 7.75 (1H, t, $J=8$ Hz).

Diastereomer A is assigned the (1R)-cis- α -R/- (1S)-cis- α -S configuration and diastereomer B is assigned the (1R)-cis- α -S/(1S)-cis- α -R configuration.

Example 11

1-R-cis-[1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate

Application of the procedure of Example 1 (Step D) with 4.5 g of 1-R-cis-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarbonyl chloride afforded 3.59 g of the title compound as a yellow oil. The ^1H NMR indicated the product consisted of a 1:1 mixture of diastereomers. ^1H NMR ($CDCl_3$) δ 1.15, 1.25, 1.27, 1.29 (4 x s, 6H), 2.02 (m, 2H), 6.03 (m, 1H), 6.65 (m, 1H), 6.85 (d, 1H), 7.1-7.5 (m, 6H), 7.78 (m, 1H). IR (neat) 1745 cm^{-1} .

Example 12

1-R-cis-[1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 2,2-dimethyl-3-(1,2,2,2-tetrabromoethyl)-cyclopropanecarboxylate

A solution of 1.76 g (3.2 mmol) of the ester of Example 11 in 10 ml of carbon tetrachloride was cooled to 0°C under N₂. To this solution was added 0.2 ml (3.9 mmol) of bromine and the reaction was then warmed to room temperature. After five days solvent and excess bromine were removed in vacuo affording the title compound as a viscous oil. ¹H NMR analysis indicated a four component mixture of diastereomers. ¹H NMR (CDCl₃) δ 1.1-1.5 (m, 6H), 1.9-2.1 (m, 2H), 4.9-5.4 (m, 1H), 6.1 (m, 1H), 6.9 (m, 1H), 7.1-7.9 (m, 7H). IR (neat) 1730 cm⁻¹.

Example 13

[1-(6-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 2,2,3,3-tetramethylcyclopropanecarboxylate

Application of the procedure of Example 1 (Step D) with 1.0 g of 2,2,3,3-tetramethylcyclopropane carbonyl chloride afforded 1.0 g of the title compound as a yellow oil. ¹H NMR (CDCl₃) δ 1.16 (s, 3H), 1.21 (s, 3H), 1.23 (s, 6H), 1.38 (s, 1H), 6.06 (q, 1H), 6.86 (d, 1H), 7.1-7.5 (m, 6H), 5 (t, 1H). IR (neat) 1750 cm⁻¹.

Example 14

[1-(5-Phenoxy-3-pyridinyl)-2,2,2-trifluoroethyl] cis-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate

To a stirred solution of 265 mg (1.09 mmol) of cis-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid, 265 mg (0.984 mmol) of 5-phenoxy-α-trifluoromethyl-3-pyridine-methanol, and 15 mg (0.22 mmol) of 4-dimethylamino-pyridine (DMAP) in 3.0 ml of CH₂Cl₂ cooled to 0°C

under a nitrogen atmosphere was added 254 mg (1.23 mmol) of 1,3-dicyclohexylcarbodiimide (DCC). After 1 hour at 0°C, the mixture was diluted with 20 ml of hexane and filtered. The filtrate was concentrated under reduced pressure and chromatography of the residue on 50 g of silica gel with 1:20 ethyl acetate/hexane afforded first 227 mg (47%) of diastereomer A assigned the (1R)-cis- α -R/(1S)-cis- α -S configuration: R_f = 0.10 (silica gel, 1:20 ethyl acetate/hexane); ^1H NMR (CDCl_3) δ 1.29 (s, 3H), 1.36 (s, 3H), 2.11 (d, 8.2 Hz, 1H), 2.25 (t, 8.6 Hz, 1H), 6.17 (q, 6.2 Hz, 1H), 6.76 (d, 9.3 Hz, 1H), 7.04 (d, 8.6 Hz, 2H), 7.21 (m, 1H), 7.40 (t, 8.0 Hz, 2H), 7.40 (s, 1H), and 8.43 (s, 2H).

Further elution then afforded 206 mg (42%) of diastereomer B, assigned the (1R)-cis- α -S/(1S)-cis- α -R configuration: R_f = 0.06 (SiO_2 , 1:20 ethyl acetate/hexane); ^1H NMR (CDCl_3) δ 1.17 (s, 3H), 1.32 (s, 3H), 2.13 (d, 8.2 Hz, 1H), 2.28 (t, 8.6 Hz, 1H), 6.10 (q, 6.9 Hz, 1H), 6.78 (d, 9.0 Hz, 1H), 7.05 (d, 8.3 Hz, 2H), 7.21 (m, 1H), 7.37 (s, 1H), 7.41 (t, 8.0 Hz, 2H), and 8.43 (s, 2H).

Example 15

[1-(2-Phenoxy-4-pyridinyl)-2,2,2-trifluoroethyl] cis-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate

Application of the procedure in Example 8 (Step C) with 215 mg (0.886 mmol) of the carboxylic acid, 215 mg (0.799 mmol) of 2-phenoxy- α -trifluoromethyl-4-pyridinemethanol, 12 mg (0.098 mmol) of DMAP, and 206 mg (0.998 mmol) of DCC in 2.4 ml of CH_2Cl_2 cooled to 0°C afforded, after workup and chromatography, first 184 mg (47%) of diastereomer A, assigned the (1R)-cis- α -R/(1S)-cis- α -S configuration: R_f = 0.12 (SiO_2 , 1:20 ethyl acetate:hexane); ^1H NMR (CDCl_3) δ 1.32 (s,

3H), 1.38 (s, 3H), 2.17 (d, 8.1 Hz, 1H), 2.28 (t, 8.6 Hz, 1H), 6.14 (q, 6.6 Hz, 1H), 6.77 (d, 9.0 Hz, 1H), 7.03 (s, 1H), 7.06 (d, 5.0 Hz, 1H), 7.15 (d, 7.3 Hz, 2H), 7.23 (m, 1H), 7.43 (t, 8.0 Hz, 2H), and 8.23 (d, 5.0 Hz, 1H); and then 171 mg (43%) of diastereomer B, assigned the (1R)-cis- α -S/(1S)-cis- α -R configuration: R_f = 0.08 (SiO₂, 1:20 ethyl acetate/hexane); ¹H NMR (CDCl₃) δ 1.21 (s, 3H), 1.36 (s, 3H), 2.18 (d, 8.1 Hz, 1H), 2.32 (t, 8.6 Hz, 1H), 6.07 (q, 6.7 Hz, 1H), 6.80 (d, 9.0 Hz, 1H), 7.00 (s, 1H), 7.05 (d, 5.0 Hz, 1H), 7.15 (d, 8.6 Hz, 2H), 7.24 (m, 1H), 7.43 (t, 7.8 Hz, 2H), and 8.24 (d, 5.0 Hz, 1H).

Example 16

[1-(4-Phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-carboxylate

To a stirred solution of 280 mg (1.04 mmol) of 4-phenoxy- α -trifluoromethyl-2-pyridinemethanol and 0.29 ml (210 mg, 2.08 mmol) of triethylamine in 2.6 ml of CH₂Cl₂ cooled to 0°C under a nitrogen atmosphere was added 284 mg (1.25 mmol) of cis-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarbonyl chloride. After 1 hour at 0°C, the reaction mixture was allowed to warm to room temperature for 15 hours. The mixture was then diluted with 60 ml of saturated aqueous NaHCO₃ and extracted with CH₂Cl₂ (2 x 25 ml). After being dried (MgSO₄), the combined extracts were concentrated under reduced pressure and chromatography of the residue on 50 g of silica gel with 1:15 ethyl acetate/hexane afforded first 215 mg (45%) of diastereomer A, assigned the (1R)-cis- α -R/(1S)-cis- α -S configuration: R_f = 0.12 (SiO₂, 1:15 ethyl acetate/hexane); ¹H NMR (CDCl₃) δ 1.26 (s, 3H), 1.30 (s, 3H), 2.03 (d, 8.0 Hz, 1H), 2.13 (t, 8.0 Hz, 1H), 6.11 (d, 8.1 Hz, 1H), 6.17 (q, 6.6 Hz, 1H), 6.82 (dd,

2.4 Hz, 6.0 Hz, 1H), 7.08 (br s, 1H), 7.11 (d, 8.1 Hz, 2H), 7.29 (m, 1H), 7.46 (t, 7.7 Hz, 2H), and 8.47 (d, 6.0 Hz, 1H).

Further elution then afforded 185 mg (39%) of
 5 diastereomer B, assigned the (1R)-cis- α -S/(1S)-cis- α -R configuration: R_f = 0.08 (SiO₂, 1:15 ethyl acetate/hexane); ¹H NMR (CDCl₃) δ 1.14 (s, 3H), 1.26 (s, 3H), 2.03 (d, 8.0 Hz, 1H), 2.14 (t, 8.0 Hz, 1H), 6.10 (q, 7.3 Hz, 1H), 6.19 (d, 8.0 Hz, 1H), 6.82
 10 (dd, 2.3 Hz, 5.3 Hz, 1H), 7.03 (br s, 1H), 7.10 (d, 8.6 Hz, 2H), 7.29 (m, 1H), 7.46 (t, 8.2 Hz, 2H), and 8.48 (d, 5.2 Hz, 1H).

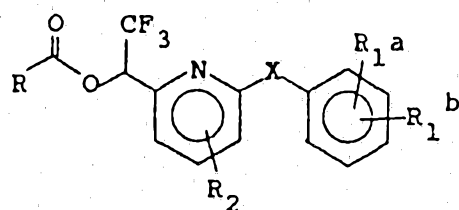
By the general procedure described herein, one
 can prepare the compounds of Tables 1 to 9 (insecti-
 15 cides and acaricides) and Tables 10 and 11 (inter-
 mediates).

20

25

30

35

General Structures for Tables 1 to 9TableR

1	R-A
2	R-B
3	R-C
4	R-D
5	R-E
6	R-F

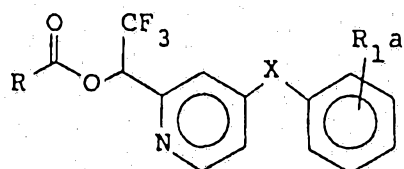
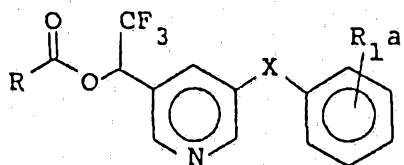
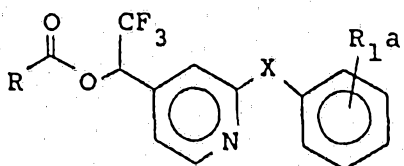
Table 7Table 8Table 9

Table 1

	<u>X</u>	<u>R₁^a</u>	<u>R₁^b</u>	<u>R₂</u>	<u>R₃</u>	<u>R₄</u>	Cyclo- propane Geometry	Phys. Prop.
5	O	4-Cl	H	H	Cl	Cl	cis/trans	
	O	4-F	H	H	Cl	Cl	cis/trans	
	O	4-Br	H	H	Cl	Cl	cis/trans	
	O	4-CF ₃	H	H	Cl	Cl	cis/trans	
	O	4-SCH ₃	H	H	Cl	Cl	cis/trans	
10	O	4-S-n-C ₄ H ₉	H	H	Cl	Cl	cis/trans	
	O	4-OCH ₃	H	H	Cl	Cl	cis/trans	
	O	3-F	H	H	Cl	Cl	cis/trans	
	O	2-Cl	H	H	Cl	Cl	cis/trans	
	O	4-Cl	H	H	CF ₃	Cl	cis/trans	oil
15	O	4-CF ₃	H	H	CF ₃	Cl	cis/trans	
	O	3-SO ₂ CH ₃	H	H	CF ₃	Cl	cis/trans	
	O	4-F	H	H	CF ₃	Cl	cis/trans	oil
	O	3-F	H	H	CF ₃	Cl	cis/trans	oil
	O	2-F	H	H	CF ₃	Cl	cis/trans	oil
20	O	H	H	H	Br	Br	cis/trans	
	O	4-F	H	H	Br	Br	cis/trans	
	O	4-Cl	H	H	Br	Br	cis/trans	
	O	4-Br	H	H	Br	Br	cis/trans	
	O	4-SCH ₃	H	H	Br	Br	cis/trans	
25	O	4-CH ₃	H	H	Br	Br	cis/trans	
	O	H	H	4-F	Cl	Cl	cis/trans	
	O	H	H	5-F	CF ₃	Cl	cis/trans	
	O	H	H	3-Cl	CF ₃	Cl	cis/trans	
	O	H	H		CO ₂ CH ₃	Cl	cis/trans	
30	O	4-Cl	H	H	CO ₂ CH ₃	Cl	cis/trans	
	O	4-CH ₃	H	H	CO ₂ CH ₃	Cl	cis/trans	
	O	4-F	H	H	CO ₂ C ₂ H ₅	Cl	cis/trans	
	O	H	H	H	CO ₂ C ₂ H ₅	Cl	cis/trans	
35	O	H	H	H	CH ₃	CH ₃	cis/trans	

Table 1 (continued)

	X	R ₁ ^a	R ₁ ^b	R ₂	R ₃	R ₄	Cyclo- propane Geometry	Phys. Prop.
5	O	4-SCH ₃	H	H	CH ₃	CH ₃	cis/trans	
	O	4-O-n-C ₄ H ₉	H	H	Cl	Cl	cis/trans	
	O	4-OCF ₂ H	H	H	Cl	Cl	cis/trans	
	O	4-OCF ₂ CF ₂ H	H	H	Cl	Cl	cis/trans	
	O	4-SCF ₂ H	H	H	Cl	Cl	cis/trans	
10	O	4-Cl	3-Cl	H	CF ₃	Cl	cis/trans	
	O	4-Cl	2-F	H	CF ₃	Cl	cis/trans	
	O	4-CH ₃	2-Cl	H	CF ₃	Cl	cis/trans	
	O	4-OCH ₃	3-OCH ₃	H	CF ₃	Cl	cis/trans	
	O	3,4-OCH ₂ O-		H	Br	Br	cis/trans	
15	O	4-OCH ₂ CH ₂ Cl	H	H	Br	Br	cis/trans	
	O	4-OCF ₂ CF ₂ H	H	H	Br	Br	cis/trans	
	S	H	H	H	Cl	Cl	cis/trans	
	S	H	H	H	CF ₃	Cl	cis/trans	
	S	H	H	H	Br	Cl	cis/trans	
20	S	H	H	H	CH ₃	CH ₃	cis/trans	
	S	H	H	H	Br	Br	cis/trans	
	O	H	H	5-Cl	Cl	Cl	cis/trans	
	O	H	H	5-Cl	CF ₃	Cl	cis/trans	
	O	H	H	5-F	Cl	Cl	cis/trans	
25	O	H	H	5-Cl	Br	Br	cis/trans	
	O	H	H	5-F	Br	Br	cis/trans	
	O	2-Cl	4-F	H	CF ₃	Cl	cis/trans	oil
	O	4-OCH ₃	H	H	CF ₃	Cl	cis/trans	oil
	O	4-SCH ₃	H	H	CF ₃	Cl	cis/trans	IR
30	O	3-Cl	H	H	Cl	Cl	cis/trans	1752 cm ⁻¹
	O	3-Cl	H	H	CF ₃	Cl	cis/trans	
	O	2-F	H	H	Cl	Cl	cis/trans	

35

Table 1 (continued)

	<u>X</u>	<u>R₁^a</u>	<u>R₁^b</u>	<u>R₂</u>	<u>R₃</u>	<u>R₄</u>	Cyclo- propane Geometry	Phys. Prop.
5	O	4-Cl	H	H	Cl	Cl	cis	oil
	O	4-F	H	H	Cl	Cl	cis	m.p. 69° to 72°C
	O	4-Br	H	H	Cl	Cl	cis	
	O	4-CF ₃	H	H	Cl	Cl	cis	
10	O	4-SCH ₃	H	H	Cl	Cl	cis	IR 1748 cm ⁻¹
	O	4-S-n-C ₄ H ₉	H	H	Cl	Cl	ci	
	O	4-OCH ₃	H	H	Cl	Cl	cis	oil
	O	3-F	H	H	Cl	Cl	cis	oil
15	O	2-Cl	H	H	Cl	Cl	cis	IR 1745 cm ⁻¹
	O	4-Cl	H	H	CF ₃	Cl	cis	
	O	4-CF ₃	H	H	CF ₃	Cl	cis	
	O	3-SO ₂ CH ₃	H	H	CF ₃	Cl	cis	
	O	4-F	H	H	CF ₃	Cl	cis	oil
	O	3-F	H	H	CF ₃	Cl	cis	oil
20	O	2-F	H	H	CF ₃	Cl	cis	oil
	O	H	H	H	Br	Br	cis	
	O	4-F	H	H	Br	Br	cis	
	O	4-Cl	H	H	Br	Br	cis	
	O	4-Br	H	H	Br	Br	cis	
25	O	4-SCH ₃	H	H	Br	Br	cis	
	O	4-CH ₃	H	H	Br	Br	cis	
	O	H	H	4-F	Cl	Cl	cis	
	O	H	H	5-F	CF ₃	Cl	cis	
	O	H	H	3-Cl	CF ₃	Cl	cis	
30	O	H	H	H	CO ₂ CH ₃	Cl	cis	
	O	4-Cl	H	H	CO ₂ CH ₃	Cl	cis	
	O	4-CH ₃	H	H	CO ₂ CH ₃	Cl	cis	
	O	4-F	H	H	CO ₂ C ₂ H ₅	Cl	cis	
	O	H	H	H	CO ₂ C ₂ H ₅	Cl	cis	
35	O	H	H	H	CH ₃	CH ₃	cis	

Table 1 (continued)

	<u>X</u>	<u>R₁^a</u>	<u>R₁^b</u>	<u>R₂</u>	<u>R₃</u>	<u>R₄</u>	Cyclo- propane Geometry	Phys. Prop.
5	O	4-SCH ₃	H	H	CH ₃	CH ₃	cis	
	O	4-O-n-C ₄ H ₉	H	H	Cl	Cl	cis	
	O	4-OCF ₂ H	H	H	Cl	Cl	cis	
	O	4-OCF ₂ CF ₂ H	H	H	Cl	Cl	cis	
	O	4-SCF ₂ H	H	H	Cl	Cl	cis	
10	O	4-Cl	3-Cl	H	CF ₃	Cl	cis	
	O	4-Cl	2-F	H	CF ₃	Cl	cis	
	O	4-CH ₃	2-Cl	H	CF ₃	Cl	cis	
	O	4-OCH ₃	3-OCH ₃	H	CF ₃	Cl	cis	
	O	3,4-OCH ₂ O-	H	H	Br	Br	cis	
15	O	4-OCH ₂ CH ₂ Cl	H	H	Br	Br	cis	
	O	4-OCF ₂ CF ₂ H	H	H	Br	Br	cis	
	S	H	H	H	Cl	Cl	cis	
	S	H	H	H	CF ₃	Cl	cis	
	S	H	H	H	Br	Cl	cis	
20	S	H	H	H	CH ₃	CH ₃	cis	
	S	H	H	H	Br	Br	cis	
	O	H	H	5-Cl	Cl	Cl	cis	
	O	H	H	5-Cl	CF ₃	Cl	cis	
	O	H	H	5-F	Cl	Cl	cis	
25	O	H	H	5-Cl	Br	Br	cis	
	O	H	H	5-F	Br	Br	cis	
	O	2-Cl	4-F	H	CF ₃	Cl	cis	
	O	4-OCH ₃	H	H	CF ₃	Cl	cis	
	O	4-SCH ₃	H	H	CF ₃	Cl	cis	
30	O	3-Cl	H	H	Cl	Cl	cis	IR 1746 cm ⁻¹
	O	3-Cl	H	H	CF ₃	Cl	cis	IR 1750 cm ⁻¹
	O	2-F	H	H	Cl	Cl	cis	oil
	O	2-Cl	H	H	CF ₃	Cl	cis	IR 1750 cm ⁻¹

Table 1 (continued)

	X	R ₁ ^a	R ₁ ^b	R ₂	R ₃	R ₄	Cyclo- propane Geometry	Phys. Prop.
5	O	4-Cl	H	H	Cl	Cl	trans	
	O	4-F	H	H	Cl	Cl	trans	
	O	4-Br	H	H	Cl	Cl	trans	
	O	4-CF ₃	H	H	Cl	Cl	trans	
	O	4-SCH ₃	H	H	Cl	Cl	trans	
10	O	4-S-n-C ₄ H ₉	H	H	Cl	Cl	trans	
	O	4-OCH ₃	H	H	Cl	Cl	trans	
	O	3-F	H	H	Cl	Cl	trans	
	O	2-Cl	H	H	Cl	Cl	trans	
	O	4-Cl	H	H	CF ₃	Cl	trans	
15	O	4-CF ₃	H	H	CF ₃	Cl	trans	
	O	3-SO ₂ CH ₃	H	H	CF ₃	Cl	trans	
	O	4-F	H	H	CF ₃	Cl	trans	
	O	3-F	H	H	CF ₃	Cl	trans	
	O	2-F	H	H	CF ₃	Cl	trans	
20	O	H	H	H	Br	Br	trans	
	O	4-F	H	H	Br	Br	trans	
	O	4-Cl	H	H	Br	Br	trans	
	O	4-Br	H	H	Br	Br	trans	
	O	4-SCH ₃	H	H	Br	Br	trans	
25	O	4-CH ₃	H	H	Br	Br	trans	
	O	H	H	4-F	Cl	Cl	trans	
	O	H	H	5-F	CF ₃	Cl	trans	
	O	H	H	3-Cl	CF ₃	Cl	trans	
	O	H	H	H	CO ₂ CH ₃	Cl	trans	
30	O	4-Cl	H	H	CO ₂ CH ₃	Cl	trans	
	O	4-CH ₃	H	H	CO ₂ CH ₃	Cl	trans	
	O	4-F	H	H	CO ₂ C ₂ H ₅	Cl	trans	
	O	H	H	H	CO ₂ C ₂ H ₅	Cl	trans	
35	O	H	H	H	CH ₃	CH ₃	trans	

Table 1 (continued)

	X	R ₁ ^a	R ₁ ^b	R ₂	R ₃	R ₄	Cyclo- propane Geometry	Phys. Prop.
5	O	4-SCH ₃	H	H	CH ₃	CH ₃	trans	
	O	4-O-n-C ₄ H ₉	H	H	Cl	Cl	trans	
	O	4-OCF ₂ H	H	H	Cl	Cl	trans	
	O	4-OCF ₂ CF ₂ H	H	H	Cl	Cl	trans	
	O	4-SCF ₂ H	H	H	Cl	Cl	trans	
10	O	4-Cl	3-Cl	H	CF ₃	Cl	trans	
	O	4-Cl	2-F	H	CF ₃	Cl	trans	
	O	4-CH ₃	2-Cl	H	CF ₃	Cl	trans	
	O	4-OCH ₃	3-OCH ₃	H	CF ₃	Cl	trans	
	O	3,4-OCH ₂ O-		H	Br	Br	trans	
15	O	4-OCH ₂ CH ₂ Cl	H	H	Br	Br	trans	
	O	4-OCF ₂ CF ₂ H	H	H	Br	Br	trans	
	S	H	H	H	Cl	Cl	trans	
	S	H	H	H	CF ₃	Cl	trans	
	S	H	H	H	Br	Cl	trans	
20	S	H	H	H	CH ₃	CH ₃	trans	
	S	H	H	H	Br	Br	trans	
	O	H	H	5-Cl	Cl	Cl	trans	
	O	H	H	5-Cl	CF ₃	Cl	trans	
	O	H	H	5-F	Cl	Cl	trans	
25	O	H	H	5-Cl	Br	Br	trans	
	O	H	H	5-F	Br	Br	trans	
	O	2-Cl	4-F	H	CF ₃	Cl	trans	
	O	4-OCH ₃	H	H	CF ₃	Cl	trans	
	O	4-SCH ₃	H	H	CF ₃	Cl	trans	
30	O	3-Cl	H	H	Cl	Cl	trans	
	O	3-Cl	H	H	CF ₃	Cl	trans	
	O	2-F	H	H	Cl	Cl	trans	

Table 1 (continued)

	<u>X</u>	<u>R₁^a</u>	<u>R₁^b</u>	<u>R₂</u>	<u>R₃</u>	<u>R₄</u>	Cyclo- propane Geometry	Dia.*	Phys. Prop.
5	O	H	H	H	Cl	Cl	cis	B	oil
	O	4-F	H	H	Cl	Cl	cis	B	
	O	4-Br	H	H	Cl	Cl	cis	B	
	O	4-CF ₃	H	H	Cl	Cl	cis	B	
	O	4-SCH ₃	H	H	Cl	Cl	cis	B	
10	O	4-S-n-C ₄ H ₉	H	H	Cl	Cl	cis	B	
	O	4-OCH ₃	H	H	Cl	Cl	cis	B	
	O	3-F	H	H	Cl	Cl	cis	B	
	O	2-Cl	H	H	Cl	Cl	cis	B	
	O	4-Cl	H	H	CF ₃	Cl	cis	B	
15	O	4-CF ₃	H	H	CF ₃	Cl	cis	B	
	O	3-SO ₂ CH ₃	H	H	CF ₃	Cl	cis	B	
	O	4-F	H	H	CF ₃	Cl	cis	B	m.p. 71.5° to 74°C
	O	3-F	H	H	CF ₃	Cl	cis	B	
20	O	2-F	H	H	CF ₃	Cl	cis	B	
	O	H	H	H	Br	Br	cis	B	
	O	4-F	H	H	Br	Br	cis	B	
	O	4-Cl	H	H	Br	Br	cis	B	
	O	4-Br	H	H	Br	Br	cis	B	
25	O	4-SCH ₃	H	H	Br	Br	cis	B	
	O	4-CH ₃	H	H	Br	Br	cis	B	
	O	H	H	4-F	Cl	Cl	cis	B	
	O	H	H	5-F	CF ₃	Cl	cis	B	
	O	H	H	3-Cl	CF ₃	Cl	cis	B	
30	O	H	H	H	CO ₂ CH ₃	Cl	cis	B	
	O	4-Cl	H	H	CO ₂ CH ₃	Cl	cis	B	
	O	4-CH ₃	H	H	CO ₂ CH ₃	Cl	cis	B	
	O	4-F	H	H	CO ₂ C ₂ H ₅	Cl	cis	B	
	O	H	H	H	CO ₂ C ₂ H ₅	Cl	cis	B	
35	O	H	H	H	CH ₃	CH ₃	cis	B	

Table 1 (continued)

	X	R ₁ ^a	R ₁ ^b	R ₂	R ₃	R ₄	Cyclo- propane Geometry	Dia.*	Phys. Prop.
5	O	4-SCH ₃	H	H	CH ₃	CH ₃	cis	B	
	O	4-O-n-C ₄ H ₉	H	H	Cl	Cl	cis	B	
	O	4-OCF ₂ H	H	H	Cl	Cl	cis	B	
	O	4-OCF ₂ CF ₂ H	H	H	Cl	Cl	cis	B	
	O	4-SCF ₂ H	H	H	Cl	Cl	cis	B	
10	O	4-Cl	3-Cl	H	CF ₃	Cl	cis	B	
	O	4-Cl	2-F	H	CF ₃	Cl	cis	B	
	O	4-CH ₃	2-Cl	H	CF ₃	Cl	cis	B	
	O	4-OCH ₃	3-OCH ₃	H	CF ₃	Cl	cis	B	
	O	3,4-OCH ₂ O-		H	Br	Br	cis	B	
15	O	4-OCH ₂ CH ₂ Cl	H	H	Br	Br	cis	B	
	O	4-OCF ₂ CF ₂ H	H	H	Br	Br	cis	B	
	S	H	H	H	Cl	Cl	cis	B	
	S	H	H	H	CF ₃	Cl	cis	B	
	S	H	H	H	Br	Cl	cis	B	
20	S	H	H	H	CH ₃	CH ₃	cis	B	
	S	H	H	H	Br	Br	cis	B	
	O	H	H	5-Cl	Cl	Cl	cis	B	
	O	H	H	5-Cl	CF ₃	Cl	cis	B	
	O	H	H	5-F	Cl	Cl	cis	B	oil
25	O	H	H	5-Cl	Br	Br	cis	B	oil
	O	H	H	5-F	Br	Br	cis	B	
	O	2-Cl	4-F	H	CF ₃	Cl	cis	B	
	O	4-OCH ₃	H	H	CF ₃	Cl	cis	B	
	O	4-SCH ₃	H	H	CF ₃	Cl	cis	B	
30	O	3-Cl	H	H	Cl	Cl	cis	B	
	O	3-Cl	H	H	CF ₃	Cl	cis	B	
	O	2-F	H	H	Cl	Cl	cis	B	

*Dia. - B represents the diastereomer containing the (1R)-cis-α-S enantiomer.



Table 2

	<u>X</u>	<u>R₁^a</u>	<u>R₁^b</u>	<u>R₂</u>	Phys. <u>Prop.</u>
5	O	H	H	H	IR 1750 cm ⁻¹
	O	4-Cl	H	H	
	O	4-F	H	H	
	O	4-CH ₃	H	H	
	O	4-SCH ₃	H	H	
10	O	4-OC ₂ H ₅	H	H	
	O	2-F	H	H	
	O	3-F	H	H	
	O	4-SCH ₂ CF ₃	H	H	
	O	4-OCH ₂ CF ₃	H	H	
15	O	4-CF ₃	H	H	
	O	4-CH ₂ CH ₂ CH ₂ CH ₂ F	H	H	
	O	4-S(O)C ₂ H ₅	H	H	
	O	4-Cl	2-Cl	H	
	O	4-F	2-F	H	
20	O	4-CH ₃	2-Br	H	
	O	H	H	4-CH ₃	
	O	H	H	3-Cl	
	O	H	H	5-F	
	O	H	H	4-F	
25	S	H	H	H	
	S	H	H	4-F	
	S	4-CF ₃	H	H	
	S	4-Cl	H	H	
	O	H	H	5-Cl	

30

35

41
Table 3

	<u>X</u>	<u>R₁^a</u>	<u>R₁^b</u>	<u>R₂</u>	<u>R₅</u>	<u>Phys. Prop.</u>
5	O	H	H	H	H	
	O	H	H	H	Cl	
	O	H	H	H	F	
	O	H	H	H	CH ₃	
	O	H	H	H	<u>t</u> -C ₄ H ₉	
10	O	H	H	H	CF ₃	
	O	4-Cl	H	H	H	
	O	4-Cl	H	H	<u>t</u> -C ₄ H ₉	
	O	4-F	H	H	Cl	
	O	4-F	H	H	C ₂ H ₅	
15	O	H	H	5-F	H	
	O	H	H	5-F	Cl	
	O	H	H	5-F	<u>t</u> -C ₄ H ₉	
	O	4-OCH ₃	3-Cl	H	<u>t</u> -C ₄ H ₉	
	O	4-Cl	3-Cl	H	<u>t</u> -C ₄ H ₉	
20	S	H	H	H	F	
	S	H	H	H	Cl	
	S	H	H	H	H	
	S	H	H	H	<u>t</u> -C ₄ H ₉	
	O	H	H	5-Cl	<u>t</u> -C ₄ H ₉	

25

30

35

Table 4

	<u>X</u>	<u>R₁^a</u>	<u>R₁^b</u>	<u>R₂</u>	<u>R₆</u>	<u>R₇</u>	<u>Phys.</u> <u>Prop.</u>
5	O	H	H	H	Br	Br	
	O	4-Cl	H	H	Br	Br	
	O	4-F	H	H	Br	Br	
	O	4-SCH ₃	H	H	Br	Br	
	O	4-CF ₃	H	H	Br	Br	
10	O	H	H	H	Cl	Cl	
	O	4-Cl	H	H	Cl	Cl	
	O	4-F	H	H	Cl	Cl	
	O	4-SCH ₃	H	H	Cl	Cl	
	O	4-CF ₃	H	H	Cl	Cl	
15	S	H	H	H	Br	Br	
	S	H	H	H	Cl	Cl	
	O	H	H	5-Cl	Br	Br	
	O	H	H	5-F	Br	Br	

20

25

30

35

Table 5

	<u>X</u>	<u>R₁^a</u>	<u>R₁^b</u>	<u>R₂</u>	<u>R₈</u>	<u>R₉</u>	Phys. <u>Prop.</u>
5	O	H	H	H	OCH ₃	H	
	O	H	H	H	OC ₂ H ₅	H	
	O	H	H	H	O- <u>i</u> -C ₃ H ₇	H	
	O	H	H	H	F	H	
	O	H	H	H	Br	H	
10	O	H	H	H	CF ₃	H	
	O	H	H	H	SCH ₃	H	
	O	H	H	H	SC ₂ H ₅	H	
	O	4-Cl	H	H	Cl	H	
	O	4-Cl	H	H	OC ₂ H ₅	H	
15	O	4-Cl	H	H	SC ₂ H ₅	H	
	O	4-F	H	H	Cl	H	
	O	4-F	H	H	CF ₃	H	
	O	4-F	H	H	Br	H	
	O	H	H	H	Cl	3-Cl	
20	O	H	H	H	Cl	3-F	
	O	H	H	5-F	Cl	H	
	O	H	H	5-Cl	Cl	H	
	S	H	H	H	Cl	H	
	S	H	H	H	F	H	
25	S	H	H	H	Br	H	
	S	H	H	H	CF ₃	H	
	S	H	H	H	OC ₂ H ₅	H	

30

35

Table 6

(R₁^b = H)

	X	R ₁ ^a	R ₂	m	R ₁₀	R ₁₁	R ₁₂	R ₁₃	R ₁₄	Phys. Prop.
5	O	H	H	0	H	H	Cl	Cl	Cl	
	O	H	H	0	H	H	Cl	Cl	OCH ₃	
	O	H	H	0	H	H	Cl	Cl	OC ₂ H ₅	
	O	H	H	0	H	H	Cl	Cl	OCF ₂ H	
10	O	H	H	0	H	H	F	F	Cl	
	O	H	H	0	H	H	F	F	F	
	O	H	H	0	H	H	F	F	H	
	O	H	H	0	H	H	F	F	OCF ₂ CF ₂ H	
15	O	H	H	1	F	F	F	F	Cl	
	O	H	H	1	F	F	F	F	F	
	O	H	H	1	F	F	F	F	OC ₂ H ₅	oil
	O	H	H	1	F	F	F	F	OCF ₂ H	
20	O	H	H	1	F	F	F	F	OCF ₂ CF ₂ H	
	O	H	H	1	Cl	Cl	F	F	Cl	
	O	H	H	1	Cl	Cl	F	F	OC ₂ H ₅	
	O	H	H	1	H	H	H	H	Cl	
25	O	H	H	1	H	H	H	H	OC ₂ H ₅	
	O	4-Cl	H	0	H	H	Cl	Cl	Cl	
	O	4-F	H	0	H	H	F	F	OC ₂ H ₅	
	O	4-SCH ₃	H	1	F	F	F	F	OC ₂ H ₅	
30	O	4-F	H	1	F	F	F	F	OC ₂ H ₅	oil
	O	H	5-Cl	1	F	F	F	F	OC ₂ H ₅	
	O	H	5-F	1	F	F	F	F	OC ₂ H ₅	
	S	H	H	1	F	F	F	F	OC ₂ H ₅	

30

35

Table 7

R=R-A

	<u>X</u>	<u>R₁^a</u>	<u>R₃</u>	<u>R₄</u>	<u>Phys. Prop.</u>
5	O	4-F	Cl	Cl	
	O	4-F	CF ₃	Cl	
	O	4-Cl	Cl	Cl	
	O	4-Cl	CF ₃	Cl	
10	S	H	Cl	Cl	
	S	H	CF ₃	Cl	
	O	H	Br	Br	
	O	4-F	Br	Br	
	O	H	CO ₂ CH ₃	Cl	
15	O	4-F	CO ₂ CH ₃	Cl	
	O	H	CH ₃	CH ₃	
	O	H	CF ₃	Cl	oil

R=R-B

	<u>X</u>	<u>R₁^a</u>
25	O	H
	O	4-F
	O	4-Cl
	O	4-OCH ₃
	S	H
30	S	4-F

Table 8

R=R-A

	<u>X</u>	<u>R₁^a</u>	<u>R₃</u>	<u>R₄</u>	<u>Phys. Prop.</u>
5	O	4-F	Cl	Cl	
	O	4-F	CF ₃	Cl	
	O	4-Cl	Cl	Cl	
	O	4-Cl	CF ₃	Cl	
10	S	H	Cl	Cl	
	S	H	CF ₃	Cl	
	O	H	Br	Br	
	O	4-F	Br	Br	
	O	H	CO ₂ CH ₃	Cl	
15	O	4-F	CO ₂ CH ₃	Cl	
	O	H	CH ₃	CH ₃	
	O	H	Cl	Cl	oil

R=R-B

	<u>X</u>	<u>R₁^a</u>
	O	H
25	O	4-F
	O	4-Cl
	O	4-OCH ₃
	S	H
	S	4-F

30

35

Table 9

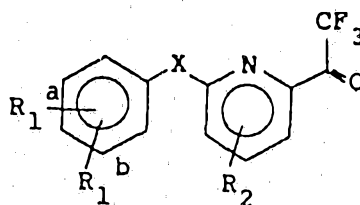
R=R-A

	<u>X</u>	<u>R₁^a</u>	<u>R₃</u>	<u>R₄</u>	<u>Phys. Prop.</u>
5	O	4-F	Cl	Cl	
	O	4-F	CF ₃	Cl	
	O	4-Cl	Cl	Cl	
	O	4-Cl	CF ₃	Cl	
10	S	H	Cl	Cl	
	S	H	CF ₃	Cl	
	O	H	Br	Br	
	O	4-F	Br	Br	
	O	H	CO ₂ CH ₃	Cl	
15	O	4-F	CO ₂ CH ₃	Cl	
	O	H	CH ₃	CH ₃	
	O	H	Cl	Cl	oil

R=R-B

	<u>X</u>	<u>R₁^a</u>
25	O	H
	O	4-F
	O	4-Cl
	O	4-OCH ₃
	S	H
30	S	4-F

Table 10



5

10

15

20

25

30

35

<u>X</u>	<u>R₁^a</u>	<u>R₁^b</u>	<u>R₂</u>	<u>Phys. Prop.</u>
O	4-Cl	H	H	IR 1740 cm ⁻¹
O	4-F	H	H	IR 1740 cm ⁻¹
O	4-Br	H	H	
O	4-CF ₃	H	H	
O	4-OCH ₃	H	H	oil
O	4-SCH ₃	H	H	IR 1740 cm ⁻¹
O	4-SO ₂ CH ₃	H	H	
O	4-OCF ₂ H	H	H	
O	2-F	4-F	H	
O	2-Cl	4-Cl	H	
O	3,4-OCH ₂ O-		H	
O	H	H	3-CH ₃	
O	H	H	4-F	
O	H	H	5-F	
S	H	H	H	m.p. 76° to 78°C
S	4-Cl	H	H	
S	4-F	H	H	
S	4-CF ₃	H	H	
O	H	H	5-Cl	
O	H	H	5-CH ₃	
O	H	H	5-Br	
O	H	H	5-CF ₃	

Table 10 (continued)

	<u>X</u>	<u>R₁</u> ^a	<u>R₁</u> ^b	<u>R₂</u>	Phys. Prop.
5	O	3-F	H	H	oil
	O	3-Cl	H	H	IR 1735 cm ⁻¹
	O	2-Cl	4-F	H	IR 1745 cm ⁻¹
	O	2-F	H	H	oil
	O	2-Cl	H	H	oil

10

15

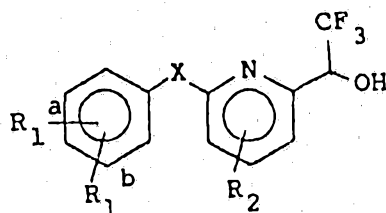
20

25

30

35

Table 11



	<u>X</u>	<u>R₁^a</u>	<u>R₁^b</u>	<u>R₂</u>	<u>Phys. Prop.</u>
5					
10	O	4-Cl	H	H	m.p. 69° to 71°C
	O	4-F	H	H	m.p. 42° to 44°C
	O	4-Br	H	H	
	O	4-CF ₃	H	H	
	O	4-OCH ₃	H	H	m.p. 98° to 101°C
15	O	4-SCH ₃	H	H	m.p. 79° to 81°C
	O	4-SO ₂ CH ₃	H	H	
	O	4-OCF ₂ H	H	H	
	O	2-F	4-F	H	
	O	2-Cl	4-Cl	H	
20	O	3,4-OCH ₂ O-		H	
	O	H	H	3-CH ₃	
	O	H	H	4-F	
	O	H	H	5-F	
	S	H	H	H	m.p. 79° to 80.5°C
25	S	4-Cl	H	H	
	S	4-F	H	H	
	S	4-CF ₃	H	H	
	O	H	H	5-Cl	
	O	H	H	5-CH ₃	
30	O	H	H	5-Br	
	O	H	H	5-CF ₃	
	O	3-F	H	H	oil
	O	3-Cl	H	H	m.p. 85° to 87°C
	O	2-Cl	4-F	H	oil
35	O	2-F	H	H	oil
	O	2-Cl	H	H	oil

Utility

The compounds of the present invention exhibit activity against a wide spectrum of foliar and soil inhabiting insects and mites. Some of the compounds of the invention surprisingly retain activity in the soil. Those skilled in the art will recognize that not all compounds are equally effective against all insects or mites, but compounds of this invention display control of many of the economically important pest species of the insect orders Lepidoptera, Homoptera, and Coleoptera among many others as well as important mite species of the order Acari. The specific species, for which control is exemplified below, are: fall armyworm, Spodoptera frugiperda; tobacco budworm, Heliothis virescens; boll weevil, Anthonomus grandis; European corn borer, Ostrinia nubilalis; southern corn rootworm, Diabrotica undecimpunctata howardi; aster leafhopper, Macrosteles fascifrons; black bean aphid, Aphis fabae; and the two-spotted spider mite Tetranychus urticae. The pest control afforded by the compounds of the present invention is not limited, however, to these species.

Formulation and Use

The compounds of this invention will generally be used in formulation with a liquid or solid diluent or with an organic solvent carrier. Useful formulations of the compounds of Formula I can be prepared in conventional ways. They include dusts, granules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like. Many of these may be applied directly. Sprayable formulations can be extended in suitable media and used at spray volumes of from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for

further formulation. The formulations, broadly, contain about 1% to 99% by weight of active ingredient(s) and at least one of a) about 0.1% to 20% surfactant(s) and b) about 5% to 99% solid or liquid diluent(s). More specifically, they will contain these ingredients in the following approximate proportions:

	Active Ingredient	<u>Percent by Weight</u>	
		<u>Diluent(s)</u>	<u>Surfactant(s)</u>
10			
	Wettable Powders	25-90	0-74
	Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	5-50	40-95
			1-10
			0-15
15	Dusts	1-25	70-99
	Granules and Pellets	1-95	5-99
	High Strength Compositions	90-99	0-10
			0-5
			0-15
			0-2

Lower or higher levels of active ingredient can, of course, be present depending on the intended use and the physical properties of the compound. Higher ratios of surfactant to active ingredient are sometimes desirable, and are achieved by incorporation into the formulation or by tank mixing.

25 Typical solid diluents are described in Watkins, et al., "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Dorland Books, Caldwell, New Jersey. The more absorptive diluents are preferred for wettable powders and the denser ones for dusts.

30 Typical liquid diluents and solvents are described in Marsden, "Solvents Guide," 2nd Ed., Interscience, New York, 1950. Solubility under 0.1% is preferred for suspension concentrates; solution concentrates are preferably stable against phase separation at 0°C.

35 "McCutcheon's Detergents and Emulsifiers Annual",

Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, "Encyclopedia of Surface Active Agents", Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc. Preferably, ingredients should be approved by the U.S. Environmental Protection Agency for the use intended.

The methods of making such compositions are well known. Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer or fluid energy mill. Suspensions are prepared by wet milling (see, for example, Littler, U.S. Patent 3,060,084). Granules and pellets may be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See J. E. Browning, "Agglomeration", Chemical Engineering, December 4, 1967, pages 147 and following, and "Perry's Chemical Engineer's Handbook", 4th Ed., McGraw-Hill, New York, 1963, pages 8 to 59 and following.

Examples of useful formulations of compounds of the present invention are as follows:

Example 17

Emulsifiable Concentrate

cis-[1-(6-phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl]	
3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane	
carboxylate	30%
blend of oil soluble sulfonates	
and polyoxyethylene ethers	4%
xylene	66%

The ingredients are combined and stirred with gentle warming to speed solution. A fine screen filter is included in packaging operation to insure

the absence of any extraneous undissolved material in the product.

Example 18

Wettable Powder

- 5 [1-(6-phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl-cyclopropanecarboxylate 30%
- sodium alkyl naphthalenesulfonate 2%
- sodium ligninsulfonate 2%
- 10 synthetic amorphous silica 3%
- kaolinite 63%

The active ingredient, warmed to reduce viscosity, is sprayed onto the inert materials in a blender. After grinding in a hammer-mill, the material is re-

15 blended and sifted through a 50 mesh screen.

Example 19

Dust

- Wettable powder of Example 18 10%
- pyrophyllite (powder) 90%
- 20 The wettable powder and the pyrophyllite diluent are thoroughly blended and then packaged. The product is suitable for use as a dust.

Example 20

Granule

- 25 [1-(6-phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] 4-chloro- α -(1-methylethyl)benzeneacetate 10%
- attapulgit granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves) 90%
- 30 The active ingredient is warmed to reduce viscosity and sprayed upon dedusted and pre-warmed attapulgit granules in a double cone blender. The granules are then allowed to cool and are packaged.

Example 21Granule

	Wettable powder of Example 18	15%
	gypsum	69%
5	potassium sulfate	16%

The ingredients are blended in a rotating mixer and water sprayed on to accomplish granulation. When most of the material has reached the desired range of 0.1 to 0.42 mm (U.S.S. No. 18 to 40 sieves), the gran-
 10 ules are removed, dried, and screened. Oversize material is crushed to produce additional material in the desired range. These granules contain 4.5% active ingredient.

Example 2215 Solution

cis-[1-(6-phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl]
 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane
 carboxylate 50%
 isophorone 50%

20 The ingredients are combined and stirred to produce a solution suitable for direct, low volume application.

Compounds of Formula I can also be mixed with one
 25 or more other insecticides, fungicides, nematocides, bactericides, acaricides, or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of effective agricultural protection. In particular, it may be advantageous to
 30 combine a compound of Formula I with substances that have a synergistic or potentiating action. Typical substances are the pyrethrin synergists of which the following are examples: [2-(2-butoxyethoxy)-ethoxy]-4,5-methylenedioxy-2-propyltoluene (piperonyl
 35 butoxide), 3-hexyl-5-(3,4-methylenedioxyphenyl)-2-

cyclohexanone (piperonyl cyclonene), 2-(3,4-methylene-dioxyphenoxy)-3,6,9-trioxaundecane, 1,2-(methylene-dioxy)-4-[2-(octylsulfinyl)propyl]benzene, dipropyl-5,6,7,8-tetrahydro-7-methylnaphtho-[2,3-d]-3-dioxole-5,6-dicarboxylate, as well as propynyl ethers and propynyl oximes. Examples of other agricultural protectants with which compounds of the present invention can be mixed or formulated are:

Insecticides:

- 10 3-hydroxy-N-methylcrotonamide(dimethylphosphate)ester
(monocrotophos)
methylcarbamic acid, ester with 2,3-dihydro-2,2-dimethyl-7-benzofuranol (carbofuran)
O-[2,4,5-trichloro- α -(chloromethyl)benzyl]phosphoric
acid, O',O'-dimethyl ester (tetrachlorvinphos)
- 15 2-mercaptosuccinic acid, diethyl ester, S-ester with
thionophosphoric acid, dimethyl ester (malathion)
phosphorothioic acid, O,O-dimethyl, O-p-nitrophenyl
ester (methyl parathion)
- 20 methylcarbamic acid, ester with α -naphthol (carbaryl)
methyl O-(methylcarbamoyl)thiolacetohydroxamate
(methomyl)
N'-(4-chloro-o-tolyl)-N,N-dimethylformamidine
(chlordimeform)
- 25 O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidylphos-
phorothioate (diazinon)
octachlorocamphene (toxaphene)
O-ethyl O-p-nitrophenyl phenylphosphonothioate (EPN)
(S)- α -cyano-m-phenoxybenzyl(1R,3R)-3-(2,2-dibromo-
vinyl)-2,2-dimethylcyclopropanecarboxylate (delta-
methrin)
- 30 Methyl N',N'-dimethyl-N-[(methylcarbamoyl)oxy]-1-thio-
oxamimidate (oxamyl)
cyano(3-phenoxyphenyl)-methyl-4-chloro- α -(1-methyl-
ethyl)benzeneacetate (fenvalerate)
- 35

(3-phenoxyphenyl)methyl(+)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
(permethrin)

5 α -cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate (cypermethrin)

O-ethyl-S-(p-chlorophenyl)ethylphosphonodithioate
(profenofos)

phosphorothiolothionic acid, O-ethyl-O-[4-(methylthio)-phenyl]-S-n-propyl ester (sulprofos).

- 10 Additional insecticides are listed hereafter by their common names: triflumuron, diflubenzuron, methoprene, buprofezin, thiodicarb, acephate, azinphos-methyl, chlorpyrifos, dimethoate, fonophos, isofenphos, methidathion, methamidiphos, monocrotophos, phosmet, 15 phosphamidon, phosalone, pirimicarb, phorate, profenofos, terbufos, trichlorfon, methoxychlor, bifenthrin, biphenate, cyfluthrin, fenpropathrin, fluvalinate, flucythrinate, tralomethrin, metaldehyde and rotenone.

20 Fungicides:

methyl 2-benzimidazolecarbamate (carbendazim)

tetramethylthiuram disulfide (thiuram)

n-dodecylguanidine acetate (dodine)

manganese ethylenebisdithiocarbamate (maneb)

25 1,4-dichloro-2,5-dimethoxybenzene (chloroneb)

methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate
(benomyl)

1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4-triazole (propiconazole)

30 2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide
(cymoxanil)

1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone (triadimefon)

N-(trichloromethylthio)tetrahydrophthalimide (captan)

35 N-(trichloromethylthio)phthalimide (folpet)

1-[[[bis(4-fluorophenyl)][methyl]silyl]methyl]-1H-
1,2,4-triazole.

Nematocides:

S-methyl 1-(dimethylcarbamoyl)-N-(methylcarbamoyloxy)-
5 thioformimidate

S-methyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimi-
date

N-isopropylphosphoramidic acid, O-ethyl O'-[4-(methyl-
thio)-m-tolyl]diester (fenamiphos).

10 Bactericides:

tribasic copper sulfate
streptomycin sulfate.

Acaricides:

senecioic acid, ester with 2-sec-butyl-4,6-dinitro-
15 phenol (binapacryl)

6-methyl-1,3-dithiolo[4,5-B]quinoxalin-2-one
(oxythioquinox)

ethyl 4,4'-dichlorobenzilate (chlorobenzilate)

1,1-bis(p-chlorophenyl)-2,2,2-trichloroethanol
20 (dicofol)

bis(pentachloro-2,4-cyclopentadien-1-yl) (dienochlor)
tricyclohexyltin hydroxide (cyhexatin)

trans-5-(4-chlorophenyl)-N-cyclohexyl-4-methyl-2-oxo-
thiazolidine-3-carboxamide (hexythiazox)

25 amitraz

propargite

fenbutatin-oxide

bisclofentezin.

Biological

30 *Bacillus thuringiensis*
Avermectin B.

Application

Insects and mites are controlled and agricultural crops are protected by applying one or more of the Formula I compounds of this invention, in an effective amount, to the locus of infestation, to the area to be protected, or directly on the pests to be controlled. A preferred method of application is by spraying with spray equipment that distributes the compound on the foliage, in the soil, or to the plant part that is infested or needs to be protected. Alternatively, granular formulations of these compounds can be applied to soil or foliage or, optionally, incorporated into the soil. Either aerial or ground application can be used.

The phenoxypyridinyl compound(s) of this invention can be applied in its(their) pure state, but most often application will be of a formulation comprising one or more compounds of this invention, in an agriculturally suitable carrier or diluent. A most preferred method of application involves spraying a water dispersion or refined oil solution of the compounds.

The rate of application of the Formula I compounds required for effective control will depend on such factors as the species of insect or mite to be controlled, the pest's life stage, its size, its location, the host crop, time of year of application, ambient moisture, temperature conditions, and the like. In general, application rates of 0.05 to 2 kg of active ingredient per hectare are sufficient to provide effective control in large scale field operations under normal circumstances, but as little as 0.01 kg/hectare may be sufficient or as much as 8 kg/hectare may be required, depending upon the factors listed above.

The following Examples demonstrate the control efficacy of compounds of Formula I on specific insect and mite pests wherein Compounds 1 through 14 are the compounds of Examples 1 through 14 and the remaining 5 compounds are those identified in Table 12.

10

15

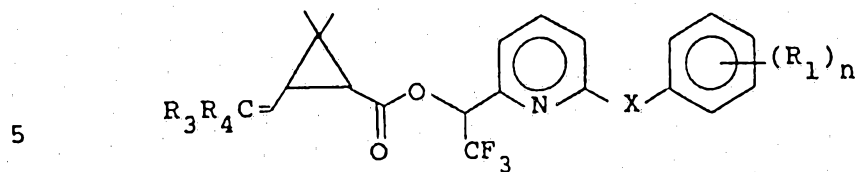
20

25

30

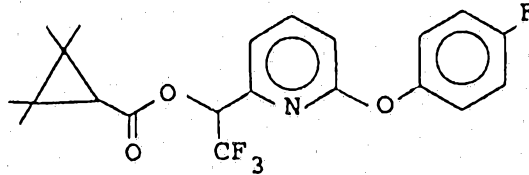
35

Table 12

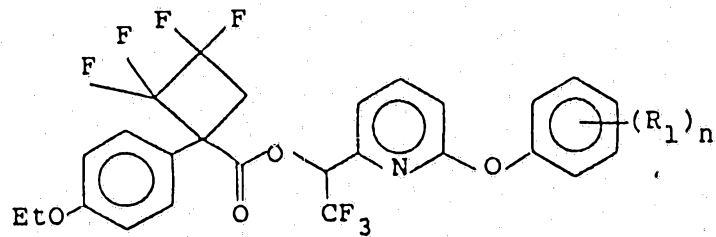


						Cyclopropane isomer composition cis/trans
10	Compound	(R ₁) _n	R ₃	R ₄	X	
	17	4-OMe	Cl	Cl	O	100/0
	18	4-OMe	CF ₃	Cl	O	30/70
	19	4-SMe	Cl	Cl	O	100/0
	20	4-SMe	CF ₃	Cl	O	30/70
15	21	4-F	CF ₃	Cl	O	40/60
	22	4-F	CF ₃	Cl	O	100/0
	23	4-Cl	Cl	Cl	O	100/0
	24	4-Cl	CF ₃	Cl	O	40/60
	25	3-F	Cl	Cl	O	100/0
20	26	3-F	CF ₃	Cl	O	30/70
	27	3-Cl	Cl	Cl	O	100/0
	28	3-Cl	CF ₃	Cl	O	100/0
	29	2-F	Cl	Cl	O	100/0
	30	2-F	CF ₃	Cl	O	30/70
25	31	2-Cl	Cl	Cl	O	100/0
	32	2-Cl	CF ₃	Cl	O	100/0
	33	2-Cl, 4-F	CF ₃	Cl	O	30/70
	34	H	Cl	Cl	S	100/0
	35	H	CF ₃	Cl	S	30/70
30	36(A)*	H	Cl	Cl	O	100/0
	36(B)*	H	Cl	Cl	O	100/0
	37(A)*	H	CF ₃	Cl	O	100/0
	37(B)*	H	CF ₃	Cl	O	100/0

Table 12 (continued)

5 Compound 38

10



15

Compound(R₁)_n

39

H

40

4-F

20 ~~* A is assigned the (1R)-cis-α-R/(1S)-cis-α-S configuration~~

~~B is assigned the (1R)-cis-α-S/(1S)-cis-α-R configuration~~

25

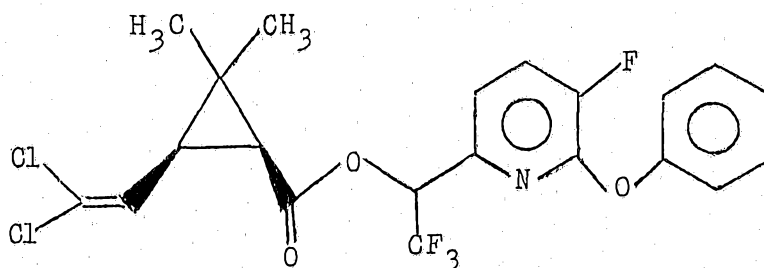
30

35



62a

Compound 41(B)*



*A is assigned the (IR)-cis- α -R/(IS)-cis- α -S configuration

B is assigned the (IR)-cis- α -S/(IS)-cis- α -R configuration



62a

Example 23Fall Armyworm

Test units, each consisting of an 8-ounce plastic cup containing a layer of wheat germ diet, approximately 0.5 cm thick, were prepared. Ten third-instar larvae of fall armyworm (Spodoptera frugiperda) were placed into each cup. Solutions of each of the below-listed test compounds (acetone/distilled water 75/25 solvent) were sprayed onto the cups, a single solution per cup. Spraying was accomplished by passing the cups, on a conveyor belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.5 pounds of active ingredient per acre (about 0.55 kg/ha) at 30 p.s.i. The cups were then covered and held at 27°C and 50% relative humidity for 72 hours, after which time mortality readings were taken. The results are tabulated below.

	<u>Compound</u>	<u>% Mortality</u> <u>72 hours post-treatment</u>
20	1	100
	2	100
	3	100
	4	100
	5A	90
25	5B	100
	6A	100
	6B	100
	7B	100
	8	100
30	9	100
	10A	27
	10B	100
	11	100
	12	100
35	13	100
	17	100
	18	100
	19	47
	20	97
	21	100
	22	100
	23	100

& Mortality
72 hours post-treatment

	<u>Compound</u>	
	24	100
	25	100
	26	100
5	27	100
	28	100
	29	100
	30	100
	31	97
	32	100
	33	65
10	34	100
	35	100
	36A	87
	36B	100
	37A	7
	37B	100
	38	100
	39	97
15	40	100
	41B	100

20

25

30

35



Example 24Tobacco Budworm

The test procedure of Example 23 was repeated for efficacy against third-instar larvae of the tobacco budworm (Heliothis virescens). The results are tabulated below.

	<u>Compound</u>	<u>% Mortality</u> <u>48 hours post-treatment</u>
10	1	100
	2	100
	3	100
	4	100
	5A	80
15	5B	100
	6A	97
	6B	97
	7B	100
	8	100
20	9	100
	10A	33
	10B	100
	11	100
	12	100
25	13	100
	17	97
	18	100
	19	87
	20	100
30	21	100
	22	100
	23	100
	24	100
	25	100
35	26	100
	27	100
	28	100
	29	100
	30	100
	31	100
	32	100
	33	67
	34	97
	35	93
	36A	50
	36B	100
	37A	3
	37B	100
	38	100
	39	93
	40	87
	41B	100



Example 25European Corn Borer

Test units, each consisting of an 8-ounce plastic cup containing a one-inch square of wheat germ/soyflour diet were prepared. Five third-instar larvae of the European corn borer (Ostrinia nubilalis) were placed into each cup. The test units were sprayed as described in Example 23 with individual solutions of the below-listed compounds. The cups were then covered and held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. The results are tabulated below.

	<u>Compound</u>	<u>% Mortality</u> <u>48 hours post-treatment</u>
15	1	100
	2	87
	3	100
	4	100
	5A	13
	5B	100
20	6A	90
	6B	100
	7B	100
	8	93
	9	100
	10A	0
	10B	100
	11	100
25	12	100
	13	100
	17	100
	18	100
	19	53
	20	67
	21	100
30	22	100
	23	93
	24	90
	25	100
	26	100
	27	100
	28	100
	29	100
35	30	100
	31	67

	<u>Compound</u>	<u>% Mortality</u> <u>48 hours post-treatment</u>
	32	100
	33	
	34	100
5	35	93
	36A	33
	36B	100
	37A	7
	37B	100
	38	100
	39	53
10	40	87

Example 26Southern Corn Rootworm

Test units, each consisting of an 8-ounce plastic cup containing 1 sprouted corn seed, were prepared. The test units were sprayed as described in Example 23 with individual solutions of the below-listed compounds. After the spray on the cups had dried, five third-instar larvae of the southern corn rootworm (Diabrotica undecimpunctata howardi) were placed into each cup. A moistened dental wick was inserted into each cup to prevent drying and the cups were then covered. The cups were then held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. The results are tabulated below.

	<u>Compound</u>	<u>% Mortality</u> <u>48 hours post-treatment</u>
	1	100
	2	60
	3	100
	4	100
5	5A	100
	5B	100
	6A	100
	6B	100
	7B	100
	8	100
	9	100
10	10A	7
	10B	100
	11	100
	12	100
	13	100
	17	100
	18	100
15	19	100
	20	100
	21	100
	22	100
	23	100
	24	100
	25	100
	26	100
20	27	87
	28	87
	29	100
	30	100
	31	80
	32	47
	33	67
25	34	100
	35	100
	36A	100
	36B	100
	37A	-
	37B	100
	38	100
	39	100
30	40	93
	41B	100

Example 27Boll Weevil

Five adult boll weevils (Anthonomus grandis)
 35 were placed into each of a series of 9-ounce cups.



The test procedure employed was then otherwise the same as in Example 23. Mortality readings taken 48 hours after treatment are tabulated below.

		<u>% Mortality</u>
	<u>Compound</u>	<u>48 hours post-treatment</u>
5	1	100
	2	100
	3	100
	4	100
	5A	47
10	5B	100
	6A	47
	6B	100
	7B	100
	8	100
15	9	100
	10A	20
	10B	93
	11	100
	12	100
20	13	73
	17	100
	18	100
	19	100
	20	100
25	21	100
	22	100
	23	100
	24	100
	25	100
30	26	100
	27	60
	28	73
	29	100
	30	100
35	31	47
	32	100
	33	-
	34	100
	35	100
	36A	73
	36B	100
	37A	0
	37B	100
	38	100
	39	100
	40	47
	41B	100



Example 28Black Bean Aphid

Test units consisting of a single nasturtium (Tropaeolum sp.) leaf infested with 5 to 10 black bean aphids (Aphis fabae) were prepared. Each leaf was cut and individually held in a 1-dram glass vial filled with a 10% sugar solution prior to and after spraying. During spraying, the infested leaves were inverted to expose the aphids, and each leaf was held in place by a clip. Leaves were sprayed with individual solutions of the below-listed compounds following the spray procedure of Example 23. Sprayed leaves were returned to the individual glass vials, covered with a clear plastic 1-ounce cup and were held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. The results are tabulated below.

	<u>Compound</u>	<u>% Mortality</u> <u>48 hours post-treatment</u>
20	1	100
	2	100
	3	100
	4	100
	5A	91
	5B	100
	6A	100
	6B	100
	7B	100
	8	100
25	9	100
	10A	100
	10B	100
	11	100
	12	100
	13	100
	17	100
	18	100
	19	100
	20	87
30	21	98
	22	100
	23	100
	24	100
35		

	<u>Compound</u>	<u>% Mortality</u> <u>48 hours post-treatment</u>
5	25	100
	26	100
	27	100
	28	100
	29	100
10	30	100
	31	99
	32	100
	33	93
	34	100
	35	96
	36A	100
	36B	100
	37A	100
	37B	100
15	38	100
	39	90
	40	90
	41B	100

Example 29Aster Leafhopper

Test units were prepared from a series of 12-ounce cups, each containing oat (Avena sativa) seedlings in a 1-inch layer of sterilized soil. The test units were sprayed as described in Example 23 with individual solutions of the below-listed compounds. After the oats had dried from the spraying, between 10 and 15 adult aster leafhoppers (Mascrosteles fascifrons) were aspirated into each of the covered cups. The cups were held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. The results are tabulated below.



Compound % Mortality
48 hours post-treatment

	1	100
	3	100
	4	100
5	5A	100
	5B	100
	6A	100
	6B	100
	7B	100
	8	100
	9	100
	10A	52
10	10B	100
	11	100
	12	100
	13	100
	17	100
	18	100
	19	85
15	20	79
	21	100
	22	100
	23	100
	24	100
	25	100
	26	100
	27	100
20	28	100
	29	100
	30	100
	31	100
	32	100
	33	100
	34	100
25	35	100
	36A	100
	36B	100
	37A	17
	37B	100
	38	100
	39	4
30	40	60
	41B	100



Example 30Soil Control of Southern Corn Rootworm

Test units, each consisting of a three-inch cylindrical pot containing 200 grams of moist sassafras loam soil and 2 kernels of Dekalb T1100 corn were prepared. Spraying was accomplished by passing the pots, on a conveyer belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.25 pounds of active ingredient per acre (about 0.275 kg/ha) at 30 p.s.i. After the test units had been sprayed, the corn seed was covered with soil and ten third-instar southern corn rootworm larvae (Diabrotica undecimpunctata howardi) were added to each unit. Test units were held at 24°C, 70% relative humidity and under a photo cycle of 16 hours of light/8 hours of darkness for 7 days, after which time control readings were taken. Control was measured by root injury ratings of 1 to 5, where 1 was no injury and 5 was complete destruction of the root system. Percent of corn seedlings that emerged also was utilized to measure control. No plant injury was observed. The results are tabulated below.

		74	
	Compound	Root injury rating	% Seedling Emergence
5	1	1.4	100
	3	1.9	88
	4	1.0	100
	5B	1.0	100
	6A	3.3	38
10	6B	1.1	100
	8	1.3	88
	9	1.5	88
	10B	1.4	100
	11	2.1	75
15	12	2.6	38
	13	1.3	88
	18	2.8	50
	19	3.5	13
	20	3.5	0
20	21	1.6	100
	22	2.1	75
	23	1.9	100
	24	2.3	75
	25	1.6	88
	26	1.3	100
	30	1.9	75
	35	3.8	0
	36B	2.8	88
	37B	1.3	100
	38	1.3	100
	41B	1.5	100

Example 31

Two-Spotted Spider Mite

Test units, each consisting of one-inch square sections of kidney bean leaves were infested with 20 to 30 adult two-spotted spider mites (Tetranychus urticae) and sprayed as described in Example 23 with individual solutions of the below-listed compounds. Sprayed leaf sections were then placed on a layer of moistened cotton in a Petri dish and held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. The results are tabulated below.



75

Compound % Mortality
48 hours post-treatment

	1	88
	2	94
	3	80
5	4	100
	5A	10
	5B	100
	6A	81
	6B	100
	7B	100
	9	100
10	10A	93
	10B	100
	11	90
	12	75
	13	95
	17	6
	18	22
	22	100
15	25	100
	26	100
	27	94
	28	100
	29	100
	30	100
	31	64
	32	100
20	34	16
	35	46
	36A	71
	36B	82
	37A	45
	37B	100
	38	100
25	40	96

30

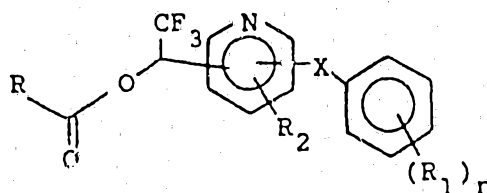
35

The claims defining the invention are as follows:-

BA-8656-A

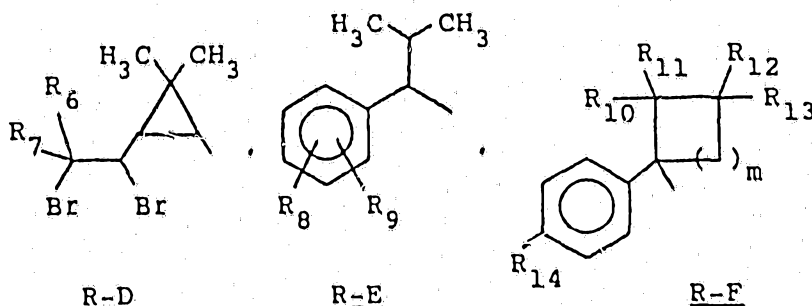
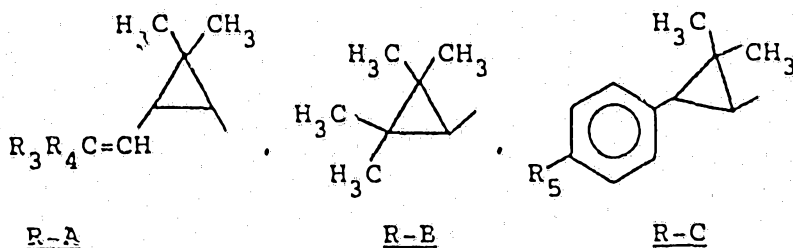
~~The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:~~

1. A phenoxy-pyridinyl compound of the formula



characterized by a 1,3-relationship between the ester and the ether substituents on the pyridine ring, wherein:

R is



X is O or S;

n is 1 to 3;

m is 0 or 1;

R₁ is H, C₁ to C₄ alkyl, C₂ to C₅ alkenyl, C₂ to C₅ alkynyl, C₁ to C₄ haloalkyl, C₁ to C₄ alkoxy, C₁ to C₄ haloalkoxy, C₁ to C₄ alkyl-



thio, C_1 to C_4 alkylsulfinyl, C_1 to C_4 alkylsulfonyl, C_1 to C_4 haloalkylthio, C_1 to C_4 haloalkylsulfonyl, F, Cl, Br; when $n = 2$, the R_1 substituents, taken together, can be 3,4-methylenedioxy;

R_2 is H, F, Cl, Br, CH_3 , or CF_3 ;

R_3 is F, Cl, Br, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl, CO_2CH_3 , or $CO_2CH_2CH_3$;

R_4 is F, Cl, Br, or CH_3 ;

R_5 is H, F, Cl, CF_3 , or C_1 to C_4 alkyl;

R_6 is Cl or Br;

R_7 is Cl or Br;

R_8 is H, C_1 to C_4 alkyl, C_1 to C_4 haloalkyl,

C_1 to C_4 alkoxy, C_1 to C_4 alkylthio, C_1 to C_4

alkylsulfinyl, C_1 to C_4 alkylsulfonyl, C_1 to

C_4 haloalkylthio, C_1 to C_4 haloalkylsulfinyl,

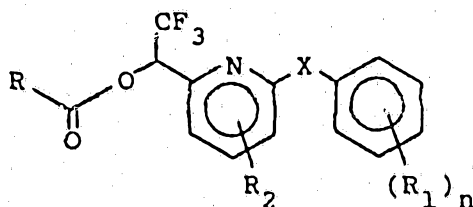
C_1 to C_4 haloalkylsulfonyl, F, Cl or Br;

R_9 is H, F, Cl, CH_3 , OCH_3 , or R_8 and R_9 , taken together, can be 3,4-methylenedioxy;

R_{10} , R_{11} , R_{12} and R_{13} are independently H, F, or Cl; and

R_{14} is H, F, Cl, OCH_3 , OCH_2CH_3 , or C_1 to C_2 haloalkoxy.

2. A compound according to Claim 1 wherein the ester and ether substituents have the 1.3 relationship shown by the formula



3. A compound according to Claim 2 wherein:

X is O;

n is 1;

m is 1;

R_1 is H, CH_3 , CF_3 , OCH_3 , OCF_2H , F, Cl, SCH_3 , SO_2CH_3 , SCF_2H , or SO_2CF_2H ;

R_2 is H, F, or Cl;

R_8 is H, F, Cl, or C_1 to C_2 alkoxy;

R_9 is H; and

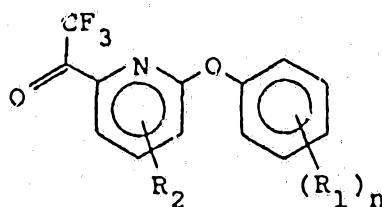
R_{14} is H, F, Cl, OCH_3 , OCH_2CH_3 or OCF_2H .

4. A compound according to Claim 3 wherein R is selected from the group consisting of R-A, R-B, R-D and R-E as hereinbefore defined.

5. A compound according to Claim 4 wherein R is R-A.

6. A compound according to Claim 4 wherein R is R-B.

7. A compound of the formula

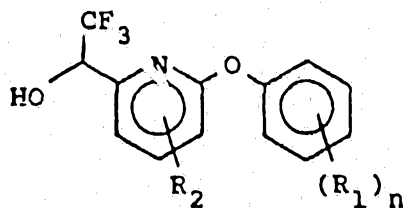


wherein:

R_1 is H, C_1 to C_4 alkyl, C_2 to C_5 alkenyl, C_2 to C_5 alkynyl, C_1 to C_4 haloalkyl, C_1 to C_4 alkoxy, C_1 to C_4 haloalkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkylsulfinyl, C_1 to C_4 alkylsulfonyl, C_1 to C_4 haloalkylthio, C_1 to C_4 haloalkylsulfonyl, F, Cl, Br; when $n = 2$, the R_1 substituents, taken together, can be 3,4-methylenedioxy;

R_2 is H, F, Cl, Br, CH_3 or CF_3 ; and n is 1 to 3.

8. A compound of the formula



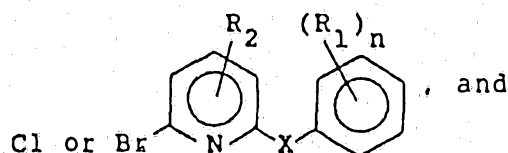
wherein:

5 R_1 is H, C_1 to C_4 alkyl, C_2 to C_5 alkenyl, C_2 to C_5 alkynyl, C_1 to C_4 haloalkyl, C_1 to C_4 alkoxy, C_1 to C_4 haloalkoxy, C_1 to C_4 alkylthio, C_1 to C_4 alkylsulfinyl, C_1 to C_4 alkylsulfonyl, C_1 to C_4 haloalkylthio, C_1 to C_4 haloalkylsulfonyl, F, Cl, Br; when $n = 2$, the R_1 substituents, taken together, can be 3,4-methylenedioxy;

10 R_2 is H, F, Cl, Br, CH_3 , or CF_3 ; and n is 1 to 3.

9. A method for making a compound according to claim 7 comprising:

15 (i) metallating the following phenoxy or thiophenoxy pyridinyl halide,



20 (ii) reacting the metallated product of step (i) with N,N-dimethyltrifluoroacetamide ($CF_3CON(CH_3)_2$) to form the corresponding phoxypyridinyltrifluoroethanone wherein: R_1 , R_2 , X and n are as previously defined.

25 10. A method according to Claim 9 comprising the additional step of reducing the ketone of step (ii).

30 11. An agricultural composition comprising a compound according to Claim 1 and an agriculturally suitable diluent or carrier.

35 12. A method for controlling pests that comprises applying to the pest or to the environment of the pest an effective amount of a compound according to Claim 1.



13. A compound according to Claim 5: cis-3-(2,2-dichloro-ethenyl)-2,2-dimethyl-cyclopropanecarboxylic acid, [1-(5-fluoro-6- phenoxy-2-pyridinyl)-2,2,2-trifluoroethyl] ester.

5

DATED this 3 day of February 1987

JAMES M. LAWRIE & CO.

By:

Patent Attorneys for

E.I. DU PONT DE NEMOURS AND COMPANY

10

15

20

25

30

35

40

