CONVENTION APPLICATION FOR A STANDARD PATENT

We, AMERICAN CYANAMID COMPANY,
of One Cyanamid Plaza, Wayne, New Jersey
United States of America
hereby apply for the grant of a standard patent for an invention entitled:
"NOVEL INSECTICIDAL DIACYLHYDRAZINE COMPOUNDS"
which is described in the accompanying complete specification.

DETAILS OF BASIC APPLICATION

Number of Basic Application:- 806,995
Name of Convention Country in which Basic Application was filed:- United States of America
Date of Basic application:- 9 December 1985
Our address for service is:-
C/- Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia
DATED this EIGHTH day of DECEMBER 1986

AMERICAN CYANAMID COMPANY

By: Registered Patent Attorney.

TO: THE COMMISSIONER OF PATENTS AUSTRALIA

SBR: ALB: 229F
In support of the Convention Application made for a patent for an invention entitled: "NOVEL INSECTICIDAL DIACYLHYDRAZINE COMPOUNDS"

I/We

JOHN J. HAGAN,

of

86 Ocean Drive East, Stamford, State of Connecticut, United States of America,

do solemnly and sincerely declare as follows:

1. I/We are the applicant(s) for the patent
   (or, in the case of an application by a body corporate)

   I am/We are authorised by

   AMERICAN CYANAMID COMPANY
   the applicant(s) for the patent to make this declaration on its/their behalf.

2. The basic application(s) as defined by Section 141 of the Act was/were made
   in United States of America
   on December 9, 1985
   by ROGER WILLIAMS ADDOR; DAVID GEORGE KUHN & DONALD PERRY WRIGHT, JR.

3. I/We are the actual inventor(s) of the invention referred to in the basic application(s)
   (or where a person other than the inventor is the applicant)

   ROGER WILLIAMS ADDOR; DAVID GEORGE KUHN & DONALD PERRY WRIGHT, JR., citizens of the United States of America

   of

   P. O. Box 347A, R.R. 1, Pennington, State of New Jersey
   08534; 2 Adrian Place, Newtown, State of Pennsylvania
   18940; and RR 1, Box 294 Bl, Woosamonsa Road, Pennington,
   State of New Jersey 08534, United States of America

   (respectively)

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

   1 Assignment dated November 18, 1985
   assigning said invention from the said inventors to the said company.

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(s) the subject of the application.

Declared at Stamford, this 14th day of July, 1986

Connecticut, U.S.A.

To: The Commissioner of Patents

John J. Hagan, Manager
Patent Law Department

11/81
1. A compound having the structural formula,

wherein R is C₂-C₆ alkyl; X, Y, M and N are each independently H, C₁-C₃ alkyl, C₁-C₃ alkoxy, C₁-C₃ alkylthio, C₁-C₃ alkylsulfinyl, C₁-C₃ alkylsulfonyl, cyano, F, Cl, Br, I, nitro, CF₃, R₁CF₂Z⁻, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N, and when taken together, X and Y may form a ring in which XY are represented by the structure,
and when taken together, M and N may form a ring in which MN are represented by the structure,

$$-\text{OCH}_2\text{O}-, \text{-OCF}_2\text{O}- \text{ or } \begin{array}{c}
\text{O} \\
\text{O}
\end{array}$$

Z is S(0)n or O; R₁ is H, F, CHF₂, CHFCl or CF₃; R₂ is C₁-C₃ alkyl, C₁-C₃ alkoxy or R₃R₄N; R₃ is H or C₁-C₃ alkyl; R₄ is H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2; with the provisos that at least one of X, Y, M or N is a substituent other than hydrogen and when M is para-nitro, at least one other of X, Y, or N must be a substituent other than hydrogen.
Name of Applicant: AMERICAN CYANAMID COMPANY

Address of Applicant: One Cyanamid Plaza, Wayne, New Jersey 07470, United States of America

Actual Inventor(s): ROGER WILLIAMS ADDOR, DAVID GEORGE KUHN and DONALD PERRY WRIGHT, JR.

Address for Service: Spruson & Ferguson, Patent Attorneys, Level 33 St Martins Tower, 31 Market Street, Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

"NOVEL INSECTICIDAL DIACYLHYDRAZONE COMPOUNDS"

The following statement is a full description of this invention, including the best method of performing it known to us.
NOVEL INSECTICIDAL DIACYLHYDRAZINE COMPOUNDS AND
NOVEL SUBSTITUTED AND UNSUBSTITUTED BENZOIC
ACID 1-ALKYL, 2-ALKYL AND 2-CYCLOALKYLHYDRAZIDES

ABSTRACT OF THE INVENTION
The present invention relates to unsubstituted di-acylhydrazine compounds and novel substituted diacylhydrazine compounds useful as insecticidal agents. These diacylhydrazines control insect populations and protect agronomic crops, trees, shrubs and ornamentals, both while growing and after harvesting, from insect attack.

Novel substituted benzoic acid 1 and 2-alkyl and 2-cycloalkylhydrazides effective as insecticides or intermediates for the preparation of insecticidal diacylhydrazides also are presented.
NOVEL INSECTICIDAL DIACYLHYDRAZINE COMPOUNDS AND
NOVEL SUBSTITUTED AND UNSUBSTITUTED BENZOIC
ACID 1-ALKYL, 2-ALKYL AND 2-CYCLOALKYLHYDRAZIDES

BACKGROUND OF THE INVENTION

The present invention relates to novel substituted diacylhydrazines and unsubstituted diacylhydrazines effective as insecticidal agents on both growing crops and harvested crops. Although certain hydrazine compounds are known, the use of said compounds as insecticides is neither taught nor suggested. For instance, Porter, Q.N. and Seif, A.E. "Mass Spectrometric Studies XI Skeletal Rearrangements in Acylhydrazines," Aust. J. Chem. 25: 523-529 (1972) disclose several 1,2-dibenzoyl-1-alkyl-hydrazines. Further, Mærekj, et al, "The Photochemistry of Sydnones and 1,3,4-oxdiazolin-2-one," Helv. Chem. Acta. 61(4): 1477-1510 (1978) reveal 4-nitrobenzoic acid 2-benzoyl-1-(1,1-diethyl)hydrazine without a utility.

Japanese patent application JA-091048 filed November 9, 1972 and published as J4 9,047,528 describes certain benzoylhydrazine derivatives as acaricidal agents without mentioning, suggesting or disclosing the use of diacylhydrazines for controlling insect attacks. Japanese patent application JP-050819 filed April 17, 1980 and published as application J5 6,147,066 relates to using N,N\textsuperscript{1}-dibenzyol-N,N\textsuperscript{1}-dialkyl-alkylenediamines for detecting blood in body fluids without any hint to insecticidal activity or ef-
fectiveness. Although Japanese patent application JA-020216 filed March 18, 1969 and published as JA-7,302,770-R describes certain N-substituted-N-phenyl-hydrazines which exhibit insecticidal and miticidal activity, this reference does not teach nor suggest that dibenzoyl-N-alkylhydrazines are effective insecticidal agents. Finally, German application DE 3228631 discloses phosphate or thiophosphate containing compounds, 1-phosphorylthioacetyl-2-acyl-hydrazines, for insecticidal, acaricidal, fungicidal and nematocidal use. Thus, it is seen that the present invention uniquely presents the present compounds as insecticidal agents.

The present invention also relates to compounds which are useful intermediates in the processing of dibenzoylhydrazines. These dibenzoylhydrazines are effective insecticidal stomach poisons and also are effective systemically in protecting living plants.

Further, the compounds of the invention are effective as insecticides themselves. These novel compounds and others have been found to control insects and protect living plants from insect attack.

**SUMMARY OF THE INVENTION**

The present invention relates to novel diacylhydrazine compounds effective as insecticidal agents on both growing and harvested crops. The invention also relates to the use of these novel compounds and unsubstituted diacylhydrazines as insecticidal agents and to intermediates thereof.

It is an object of the present invention, therefore, to provide the novel substituted, diacylhydrazine compounds. It is a further object to provide these compounds as effective insecticidal agents.

Furthermore, unsubstituted diacylhydrazines are useful and effective insecticidal agents in protecting living plants from insect attack.
It is another object of the invention to provide novel substituted benzoic acid 1-alkyl-, 2-alkyl- and 2-cycloalkylhydrazides, preferably 1 or 2-tert-butylhydrazides, as insecticides and also to provide many of said compounds useful in the preparation of dibenzoylhydrazine insecticides.

These and further objects of the invention will become apparent by the following more detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The novel diacylhydrazine compounds of this invention are illustrated by the following formula:

![Chemical Structure](image)

wherein R is C₂⁻C₆ alkyl; X, Y, M and N are each independently H, C₁⁻C₃ alkyl, C₁⁻C₃ alkoxy, C₁⁻C₃ alkylthio, C₁⁻C₃ alkylsulfinyl, C₁⁻C₃ alkylsulfonyl, cyano, F, Cl, Br, I, nitro, CF₃, R₁CF₂Z-, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N, and when taken together, X and Y may form a ring in which XY are represented by the structure:

![Ring Structure](image)

and when taken together, M and N may form a ring in which MN are represented by the structure:
Z is S(0)n or O; and R₁ is H, F, CHF₂, CHFCl or CF₃; R₂ is C₁-C₃ alkyl, C₁-C₃ alkoxy or R₃R₄N; R₃ is H or C₁-C₃ alkyl; R₄ is H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2; with the provisos that at least one of X, Y, M or N is a substituent other than hydrogen and when M is para nitro, at least one other of X, Y or N must be a substituent other than hydrogen.

 Preferably, R is -C(CH₃)₃ or -CH(CH₃)₂ with X, Y, M and N as herein defined and at least one of X, Y, M and N a substituent other than hydrogen.

 These compounds are highly effective insecticidal agents useful for controlling insect populations when applied at insecticidally-effective rates to said insects, their habitat, food supply or breeding grounds. We have also found that other compounds having the basic structure as illustrated above but wherein X, Y, M and N are each hydrogen or one of X, Y, M and N is nitro and R is as described above are also highly effective insecticidal agents. Additionally, we have discovered that both the substituted and the unsubstituted diacylhydrazines described above are especially useful for systemically protecting living plants for an extended period of active growth from attack by insects which infest said plants. Such protection may be achieved by applying to the soil or water in which said plants are growing, a systemically-effective amount of a compound having the formula:
wherein R is C₂-C₆ alkyl; X, Y, M and N are each independently H, C₁-C₃ alkyl, C₁-C₃ alkoxy, C₁-C₃ alkylthio, C₁-C₃ alkylsulfinyl, C₁-C₃ alkylsulfonyl, cyano, F, Cl, Br, I, nitro, CF₃, R₁CF₂Z⁻, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N, and when taken together, X and Y may form a ring in which XY are represented by the structure:

\[-OCH₂O-, \text{ or } \text{ or } \text{ or } \]

and when taken together, M and N may form a ring in which MN are represented by the structure:

\[-OCH₂O-, \text{ or } \text{ or } \text{ or } \]

Z is S(O)n or O; and R₁ is H, F, CHF₂, CHFC₁ or CF₃; R₂ is C₁-C₃ alkyl, C₁-C₃ alkoxy or R₃R₄N; R₃ is H or C₁-C₃ alkyl; R₄ is H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2.

More particularly, the protection of living plants may be achieved by applying to the foliage of said plants and/or to the soil or water in which they are growing, about 0.01 kg/hectare to about 10.0 kg/hectare of a diacylhydrazone as described hereinabove, preferably 0.028 kg/hectare
to 4.0 kg/hectare. If the active diacylhydrazine is applied as a dilute spray, said spray should contain from about 10 ppm to 10,000 ppm of said diacylhydrazine.

The present invention also relates to novel substituted benzoic acid 1-alkyl-, 2-alkyl- and 2-cycloalkylhydrazides, effective as insecticides, having the structure depicted by formula (II):

\[
\begin{align*}
\text{Formula (II)}
\end{align*}
\]

wherein \( R \) and \( R_6 \) are each independently hydrogen, \( C_2-C_6 \) alkyl or \( C_5-C_6 \) cycloalkyl; \( X \) and \( Y \) are each independently \( H, C_1-C_3 \) alkyl, \( C_1-C_3 \) alkoxy, \( C_1-C_3 \) alkylthio, \( C_1-C_3 \) alkylsulfinyl, \( C_1-C_3 \) alkylsulfonyl, cyano, \( F, Cl, Br, I, \) nitro, \( CF_3, R_1CF_2Z-, 1,1\text{-difluoro}-2,2\text{-dichloroethoxy, } R_2CO \) or \( R_3R_4N \) and when taken together \( X \) and \( Y \) may form a ring in which \( XY \) are represented by the structure:

\[
\begin{align*}
\text{(-OCH}_2\text{O-, -OCF}_2\text{O- or } \text{or })
\end{align*}
\]

\( Z \) is \( S(0)n \) or \( 0; R_1 \) is \( H, F, CHF_2, CHFCl \) or \( CF_3; R_2 \) is \( C_1-C_3 \) alkyl, \( C_1-C_3 \) alkoxy or \( R_3R_4\text{N}; R_3 \) is \( H \) or \( C_1-C_3 \) alkyl; \( R_4 \) is \( H, C_1-C_3 \) alkyl or \( R_5CO; R_5 \) is \( H \) or \( C_1-C_3 \) alkyl and \( n \) is 0, 1 or 2; with the provisos that when \( R \) is hydrogen, \( R_6 \) is \( C_2-C_5 \) alkyl or \( C_5-C_6 \) cycloalkyl and when \( R_6 \) is hydrogen, \( R \) is \( C_2-C_5 \) alkyl or \( C_5-C_6 \) cycloalkyl; and provided also that when \( R \) is tert-butyl and \( Y \) is chloro in the para position of the ring, \( X \) is a substituent other than hydrogen.

The novel substituted formula (II) benzoic acid 1-alkyl-, 2-alkyl- and 2-cycloalkylhydrazides, like the formula (I), 1-alkyl-, 2-alkyl- and 2-cycloalkylhydrazides, are
potent stomach poisons. As such, these formula (I) and
formula (II) hydrazides effectively control insect popula-
tions and protect plants from insect attack. Insecti-
cidally-effective amounts of the active compound can be
applied to the foliage of plants upon which the insects feed
or to the soil, water or other media in which said plants are
growing. These compounds may also be made available to the
insects in the form of baits or applied to the insects' breeding
grounds and habitat.

Additionally, many of the novel formula (II) benzoic
acid 1-alkyl-, 2-alkyl- and 2-cycloalkylhydrazides, sub-
stituted with halogen, CH₃, CF₃, -OCH₃, -OCH₂O-, OCF₂O-,
NH₂, NO₂ or -CH=CH-CH=CH-, are useful as intermediates for
the preparation of dibenzoylhydrazines which are effective
as insecticidal agents and systemic soil insecticidal
agents.

Process of Manufacture
The formula (II) benzoic acid 1-alkyl-, 2-alkyl- and
2-cycloalkylhydrazides of the present invention are de-
picted by the following structure:

wherein R and R₆ are each independently hydrogen, C₂-C₆
alkyl or C₅-C₆ cycloalkyl; X and Y are each independently H,
C₁-C₃ alkyl, C₁-C₃ alkoxy, C₁-C₃ alkylthio, C₁-C₃ alkyl-
sulfinyl, C₁-C₃ alkylsulfonyl, cyano, F, Cl, Br, I, nitro,
CF₃, R₁CF₂Z-, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or
R₃R₄N and when taken together X and Y may form a ring in which
XY are represented by the structure:
Z is $S(O)\text{n or } 0$; $R_1$ is $H$, $F$, $\text{CHF}_2$, $\text{CHFCl}$ or $\text{CF}_3$; $R_2$ is $C_1$-$C_3$ alkyl, $C_1$-$C_3$ alkoxy or $R_3R_4N$; $R_3$ is $H$ or $C_1$-$C_3$ alkyl; $R_4$ is $H$, $C_1$-$C_3$ alkyl or $R_5CO$; $R_5$ is $H$ or $C_1$-$C_3$ alkyl and $n$ is $0$, $1$ or $2$; with the provisos that when $R$ is hydrogen, $R_2$ is $C_2$-$C_5$ alkyl or $C_5$-$C_6$ cycloalkyl and when $R_6$ is hydrogen, $R$ is $C_2$-$C_5$ alkyl or $C_5$-$C_6$ cycloalkyl.

The formula (I) 2-alkyl- and 2-cycloalkylhydrazides of the invention are prepared by reacting an alkyl- or cycloalkylhydrazine hydrohalide with a benzoylhalide in the presence of aqueous base.

Generally, the alkyl or cycloalkylhydrazine hydrohalide is dispersed in an organic solvent, such as methylene chloride, ether or the like, and the resulting mixture then admixed with aqueous base. Usually, about two to six molar equivalents of base, such as sodium carbonate or sodium hydroxide, per equivalent of alkylhydrazine hydrohalide are used to achieve the benzoylation of the alkyl hydrazine. The thus-prepared mixture is then admixed with the appropriate benzoyl halide dissolved or dispersed in an organic solvent, preferably the same solvent used for dissolution of the alkyl- or cycloalkyl- hydrazine hydrohalide.

The mixture is stirred or agitated for a sufficient period of time to form the benzoic acid alkyl- cycloalkylhydrazide which is readily recovered from the mixture by separation of the aqueous phase from the organic phase and evaporation of the organic solvent from said organic phase.
The reaction is graphically illustrated below:

\[
\text{C}_1 \text{RNHNH}_2 \cdot \text{HQ} + \text{Aqueous base} \rightarrow \text{C}_1 \text{RNHNH}_2 \cdot \text{HQ}
\]

wherein Q is halogen, preferably chlorine and R, X and Y are as described for formula (I) compounds illustrated hereinabove.

The formula (II) benzoic acid, 1-alkyl and 2-cycloalkylhydrazides of this invention, depicted by the structure:

\[
\text{C}_1 \text{RNHNH}_2 \cdot \text{HQ} \rightarrow \text{C}_1 \text{RNHNH}_2 \cdot \text{HQ}
\]

wherein R is hydrogen; R6 is C2-C6 alkyl or C5-C6 cycloalkyl and X and Y are as described hereinabove, are prepared by reacting an alkylhydrazine or cycloalkylhydrazine with acetone. After the mixture is permitted to stand for a short period of time, it is treated with ether and potassium hydroxide pellets. The ether layer is separated from the mixture and evaporated to yield the 1-alkyl-2-isopropylidenehydrazide or 1-cycloalkyl-2-isopropylidenehydrazide.

The resulting 1-alkyl- or 1-cycloalkyl-2-isopropylidene hydrazide then is reacted with a benzoyl halide in
the presence of 10% sodium hydroxide to yield 1-alkyl or 1-cycloalkyl 2-isopropylidenehydrazide of benzoic acid. Hydrolysis of the thus-formed product with a dilute mineral acid such as 10% HCl in the presence of alcohol yields the 1-alkyl or 1-cycloalkylhydrazide of benzoic acid.

These reactions are illustrated as follows:

\[
R_6\text{-NHNH}_2 + CH_3\text{-CO}\text{-CH}_3 \rightarrow R_6\text{-NHNH=C(CH}_3\text{)_2}
\]

\[
R_6\text{-NHNH=C(CH}_3\text{)_2} + \begin{array}{c}
\text{CO}\text{-Cl} \\
\text{X} \\
\text{Y}
\end{array} \rightarrow \begin{array}{c}
\text{CO}\text{-N=NH=C(CH}_3\text{)_2} \\
\text{X} \\
\text{Y} \\
\text{R}_6
\end{array}
\]

\[
\begin{array}{c}
\text{CO}\text{-N=NH=C(CH}_3\text{)_2} \\
\text{X} \\
\text{Y} \\
\text{R}_6
\end{array} \rightarrow \begin{array}{c}
\text{CO}\text{-N-NH}_2 \\
\text{X} \\
\text{Y} \\
\text{R}_6
\end{array}
\]

wherein R₆, X and Y are as described hereinabove.

Preparation of the formula (II) benzoic acid alkyl- and cycloalkylhydrazides of this invention, wherein R₆ is hydrogen, also is achieved by reduction of the appropriate benzoic acid alkylidene hydrazide with hydrogen in the presence of a noble metal catalyst, such as platinum or palladium. The reaction preferably is conducted in the
presence of a lower alkyl \((C_1-C_4)\) alcohol under a blanket of hydrogen maintained at about 20 to 60 psig. The reaction is illustrated below:

\[
\begin{align*}
\text{H}_2 & \quad (\text{PtO}_2) \\
\text{CO-NH-N=H-R} & + \text{H}_2 \\
\end{align*}
\]

wherein \(R_1, X\) and \(Y\) are as described for formula (II) compounds hereinabove.

Formula (II) benzoic acid 2-alkylhydrazides and 2-cycloalkylhydrazides are useful as intermediates for the preparation of dibenzoylhydrazine compounds illustrated by formula (I), which are found to be extremely potent insect stomach poisons and systemic insecticidal agents. These dibenzoylhydrazines are effective for controlling a variety of insects including, but not limited to Lepidoptera, Homoptera, Orthoptera, Coleoptera and Diptera, and are likewise effective for protecting a variety of crops from insect attack.

The formula (I) dibenzoylhydrazine compounds have the following structure:

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{X} & \quad \text{R} \\
\text{Y} & \quad \text{N} \\
\text{M} & \quad \text{N} \\
\end{align*}
\]

wherein \(R\) is \(C_2-C_6\) alkyl or \(C_5-C_6\) cycloalkyl; \(X, Y, M\) and \(N\) are each independently \(H\), \(C_1-C_3\) alkyl, \(C_1-C_3\) alkoxy, \(C_1-C_3\)
alkylthio, C₁-C₃ alkylsulfinyl, C₁-C₃ alkylsulfonyl, cyano, F, Cl, Br, I, nitro, CF₃ or R₁CF₂Z-, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N, and when taken together, X and Y may form a ring in which XY are represented by the structure:

- OCH₂O-, -OCF₂O- or \( \begin{array}{c}
\text{O} \\
\text{C} \\
\text{F} \\
\text{O}
\end{array} \)

and when taken together, M and N may form a ring in which MN are represented by the structure:

- OCH₂O-, -OCF₂O- or \( \begin{array}{c}
\text{O} \\
\text{C} \\
\text{F} \\
\text{O}
\end{array} \)

Z is S(0)n or O; R₁ is H, F, CHF₂, CHFC₁ or CF₃; R₂ is C₁-C₃ alkyl, C₁-C₃ alkoxy or R₃R₄N; R₃ is H or C₁-C₃ alkyl; R₄ is H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2; with the provisos that at least one of X, Y, M or N is a substituent other than hydrogen and when M is para nitro, at least one other of X, Y, or N must be a substituent other than hydrogen.

These formula (I) compounds are prepared by the reacting approximately equimolar amounts of a benzoic acid alkylhydrazide and a benzoyl halide in the presence of an aprotic solvent, such as an ether, chlorinated hydrocarbon or the like and aqueous base. Generally, about two to six molar equivalents of base per equivalent of benzoic acid alkylhydrazide are sufficient to bring the reaction to completion. The reaction is graphically illustrated below:
wherein Q is halogen; and R, X, Y, M and N are as described hereinabove for formula (I).

As stated hereinabove, advantageously, the compounds of this invention can be prepared in a rather expeditious manner. In accordance with the process of this invention, a C2-C6 alkylhydrazine hydrohalide is dispersed in an organic solvent, such as methylene chloride, ether or the like, and the resulting mixture then admixed with an aqueous base. Usually, about two to six molar equivalents of base, such as sodium carbonate or sodium hydroxide, per equivalent of alkylhydrazine hydrohalide are used to achieve the benzoylation of the alkyl hydrazine. The thus-prepared mixture is then admixed with the appropriate benzoyl halide dissolved or dispersed in an organic solvent, preferably the same solvent used for dissolution of the alkylhydrazine hydrohalide.

The mixture is stirred or agitated for a sufficient period of time to form the benzoic acid alkylhydrazide which is readily recovered from the mixture by separation of the aqueous phase from the organic phase and evaporation of the organic solvent from said organic phase.

The reaction is graphically illustrated below:
wherein Q is halogen, preferably chlorine; R is C₂⁻C₆ alkyl and X and Y are each independently H, C₁⁻C₃ alkyl, C₁⁻C₃ alkoxy, C₁⁻C₃ alkylthio, C₁⁻C₃ alkylsulfinyl, C₁⁻C₃ alkylsulfonyl, cyano, F, Cl, Br, nitro, CF₃, R₁CF₂Z⁻, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N and when taken together X and Y may form a ring in which XY are represented by the structure:

Z is S(0)n or O and R₁ is H, F, CHF₂, CHFC₁ or CF₃; R₂ is C₁⁻C₃ alkyl, C₁⁻C₃ alkoxy or R₃R₄N; R₃ is H or C₁⁻C₃ alkyl and R₄ is H, C₁⁻C₃ alkyl or R₅CO; R₅ is H or C₁⁻C₃ alkyl and n is 0, 1 or 2. As used in this application, where R is C₂⁻C₆ alkyl, it is intended to include straight and branched alkyl groups C₂⁻C₆ and cycloalkyl groups C₃⁻C₆.

Preparation of the benzoic acid alkylhydrazides may also be achieved by reduction of the appropriate benzoic acid alkylidene hydrazide with hydrogen in the presence of a noble metal catalyst, such as platinum or palladium. The reaction is preferably conducted in the presence of a lower
alkyl C₁-C₄ alcohol under a blanket of hydrogen maintained at about 20 to 60 psig. The reaction is illustrated below:

\[
\text{alkyl CO-NH-NH-R} + \text{H₂} \xrightarrow{\text{PtO₂}} \text{alkyl CO-NH-NH-R}
\]

wherein R is C₂-C₆ alkyl; X and Y are each independently H, C₁-C₃ alkyl, C₁-C₃ alkoxy, C₁-C₃ alkylthio, C₁-C₃ alkylsulfinyl, C₁-C₃ alkylsulfonyl, cyano, F, Cl, Br, nitro, CF₃, R₁CF₂Z⁻, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N, and when taken together X and Y may form a ring in which XY are represented by the structure:

\[
\begin{aligned}
&\text{OCH₂O⁻, OCF₂O⁻ or } \\
&\text{OCH₂O⁻, OCF₂O⁻ or }
\end{aligned}
\]

Z is S(O)n or O and R₁ is H, F, CHF₂, CHFCl or CF₃; R₂ is C₁-C₃ alkyl, C₁-C₃ alkoxy or R₃R₄N; R₃ is H or C₁-C₃ alkyl and R₄ is H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2.

The above-described benzoic acid alkylhydrazides are useful as insecticidal agents and particularly effective when used for the control of lepidopterous insects. These compounds also have the added advantage that they are useful as intermediates for the preparation of dibenzoyl hydrazine compounds which we have found to be extremely potent insect stomach poisons and systemic insecticidal agents, effective for controlling a variety of insects including, Lepidoptera, Homoptera, Orthoptera, Coleoptera and Diptera, and are likewise effective for protecting a variety of crops from insect attack. These compounds have also been found to have some activity as contact insecticides.
The novel dibenzoyl hydrazine compounds of this invention have the structure:

\[
\begin{align*}
\text{R} & \quad \text{X} & \quad \text{Y} & \quad \text{M} & \quad \text{N} \\
\text{C}_{2}-\text{C}_{6} \text{ alkyl} & \quad \text{H, C}_{1}-\text{C}_{3} \text{ alkyl, C}_{1}-\text{C}_{3} \text{ alkoxy, C}_{1}-\text{C}_{3} \text{ alkylthio, C}_{1}-\text{C}_{3} \text{ alkylsulfinyl, C}_{1}-\text{C}_{3} \text{ alkylsulfonyl, cyano, F, Cl, Br, I, nitro, CF}_{3}, & \quad R_{1} \text{CF}_{2}Z \text{ or 1,1-difluoro-2,2-dichloroethoxy, R}_{2} \text{CO or R}_{3}R_{4}N, & \quad \text{and when taken together, X and Y may form a ring in which XY are represented by the structure:} \\
& & & & \quad \text{and when taken together, M and N may form a ring in which MN are represented by the structure:} \\
& & & & \quad \text{Z is S(O)n or O; and R}_{1} \text{ is H, F, CHF}_{2}, \text{CHFCl or CF}_{3}; R_{2} \text{ is C}_{1}-\text{C}_{3} \text{ alkyl, C}_{1}-\text{C}_{3} \text{ alkoxy or R}_{3}R_{4}N; R_{3} \text{ is H or C}_{1}-\text{C}_{3} \text{ alkyl; R}_{4} \text{ is H, C}_{1}-\text{C}_{3} \text{ alkyl or R}_{5} \text{CO; R}_{5} \text{ is H or C}_{1}-\text{C}_{3} \text{ alkyl and n is 0, 1 or 2; with the provisos that at least one of X, Y, M or N is a substituent other than hydrogen and when M is para nitro, at least one other of X, Y or N must be a substituent other than hydrogen. These are prepared by the reaction of approximately equimolar amounts of a benzoic acid alkylhydrazide and a benzoyl halide in the presence of an aprotic}
\end{align*}
\]
solvent such as an ether, chlorinated hydrocarbon or the like and aqueous base. Generally, about two to six molar equivalents of base per equivalent of benzoic acid alkylhydrazide are sufficient to bring the reaction to completion. The reaction is graphically illustrated below:

\[
\begin{align*}
\text{CO-NHN}_2 & + \text{COQ} \\
\text{CH}_2\text{Cl}_2 & \text{10% NaOH} \\
\text{CO-NH-N-CO} & \\
\end{align*}
\]

wherein \(Q\) is halogen; \(R\) is \(C_2-C_6\) alkyl, \(X, Y, M\) and \(N\) are each independently \(H, C_1-C_3\) alkyl, \(C_1-C_3\) alkoxy, \(C_1-C_3\) alkylthio, \(C_1-C_3\) alkylsulfinyl, \(C_1-C_3\) alkylsulfonyl, cyano, \(F, Cl, Br\), nitro, \(CF_3, R_1CF_2Z\), 1,1-difluoro-2,2-dichloroethoxy, \(R_2CO\) or \(R_3R_4N\), and when taken together, \(X\) and \(Y\) may form a ring in which \(XY\) are represented by the structure:

\[
\begin{align*}
\text{-OCH}_2\text{O-}, \text{-OCF}_2\text{O-} \quad \text{or} \\
\end{align*}
\]

and when taken together, \(M\) and \(N\) may form a ring in which \(MN\) are represented by the structure:

\[
\begin{align*}
\text{-OCH}_2\text{O-}, \text{-OCF}_2\text{O-} \quad \text{or} \\
\end{align*}
\]

\(Z\) is \(S(0)n\) or \(O\); and \(R_1\) is \(H, F, CHF_2, CHFC1\) or \(CF_3\); \(R_2\) is
C_1-C_3 alkyl, C_1-C_3 alkoxy or R_3R_4N; R_3 is H or C_1-C_3 alkyl and R_4 is H, C_1-C_3 alkyl or R_5CO; R_5 is H or C_1-C_3 alkyl and n is 0, 1 or 2.

Compositions with other Compounds

Although the diacylhydrazines of the present invention do not require the presence of synergists to be effective insecticidal agents, they may be used to advantage in conjunction with synergists such as 5-[1-[2-(2-ethoxyethoxy)ethoxy]ethoxy]-1,3-benzodioxole; n-(2-ethylhexyl)-5-norbornene-2,3-dicarboximide; 5-[2-(octylsulfinyl)propyl]-1,3-benzodioxole or piperonyl butoxide. They may also be used in combination or conjunction with other conventional insecticides such as pyrethroids, phosphates, carbamates, chlorinated hydrocarbons, halobenzoylureas, and formamidines.

Among the pesticides contemplated for use in conjunction with the diacylhydrazines of this invention are:

(RS)-α-cyano(3-phenoxyphenyl)methyl (RS)-4-chloro-α-(1-methylethyl)benzeneacetate;
(RS)-α-cyano(3-phenoxyphenyl)methyl (I-RS)-cis, trans-3-(2,2-dichloroethenyl)-2,2-dimethyl cyclopropane-carboxylate;
(+)-α-cyano(3-phenoxyphenyl)methyl (+)-4-(difluoromethoxy)-α-(1-methylethyl)benzeneacetate;
(3-phenoxyphenyl)methyl (I-RS-cis, trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate;
2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane;
4,4'-dichloro-α-trichloromethylbenzyhydrol;
3-(dimethoxyphosphinyloxy)-N,N-dimethyl-ciscrotonamide;
diethyl(dimethoxyphosphinothioylthio)succinate;
0,0-dimethyl O-[3-methyl-4-(methylthio)phenyl]-phosphorothioate;
S-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-yl-methyl 0,0-diethyl phosphorodithioate;
N,N-dimethyl-2-methylcarbamoyloximino-2-(methylthio)acetamide;
1-methylethyl (E,E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate;
S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-yl methyl 0,0-dimethyl phosphorodithioate;
O,S-dimethyl phosphoramidothioate;
2-(diethoxyphosphinylimino)-4-methyl-1,3-dithiolane;
(RS)-α-cyano-3-phenoxybenzyl N-(2-chloro-α,α,α-trifluorophenyl)-D-valinate;
4-chlorophenyl-3-(2,6-difluorobenzoyl)urea;
0,0-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate;
N'-(4-chloro-2-methylphenyl)-N,N-dimethylmethanimidamide;
1,3-di(carbamoylthio)-2-dimethylaminopropane;
N-methylbis(2,4-xylyliminomethyl)amine;
O,S-dimethyl acetylphospharamidithioate;
(RS-α-cyano-4-fluoro-3-phenoxybenzyl (I-RS)-cis, trans-3-(2,2-dichlorovinyl-2,2-dimethylcyclopropanecarboxylate;
S-methyl N-(methylcarbamoyloxy)thio-acetimide;
2,3-dihydro-2,2-dimethyl-7-benzofuranylmethylcarbamate;
2-methyl-2-(methylthio)propanal O-[(methylamino)carbonyl]oxime;
0,0-diethyl O-(tert-butylthiomethyl)phosphorodithioate;
0,0-dimethyl S-phthalimidomethyl phosphorodithioate;
0-2,4-dichlorophenyl O-ethyl S-propyl phosphorodithioate;
0-4-bromo-2-chlorophenyl O-ethyl S-propyl phosphorothioate;
2-(dimethylamino-5,6-dimethyl-4-pyrimidinyl dimethyldibaminate;
0,0-diethyl S-p-chlorophenylthiomethyl phosphorodithioate;
6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide;
2,4,5,4'-tetrachlorodiphenyl sulphone;
alpha-methylbenzyl 3-(dimethoxyphosphinyloxy)-cis-crotonate;
2-(2-butoxyethoxy) ethyl ester;
bis(dialkylphosphinothionyl)disulfide;
0,0-dimethyl 0-2-chloro-4-nitrophenyl phosphorodithioate;
S-α-cyano-3-phenoxybenzyl (I-R)-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate;
(+)-α-cyano-4-fluoro-3-phenoxybenzyl (+)-4-difluoromethoxy-α-(1-methylethyl)benzeneacetate;
0,0-diethyl 0-p-nitrophenyl phosphorothioate;
0,0-dimethyl 0-p-nitrophenyl phosphorothioate;
0,0-dimethyl 0-(3-methyl-4-nitrophenyl) thionophosphate;
0,0-dimethyl S-p-chlorophenylthiomethyl phosphorodithioate;
4-dimethylamino-3,5-xylyl methylcarbamate;
2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane; dichlorodiphenyl dichloroethane;
chlorinated camphene;
terpene polychlorinate;
0,0,0',0'-tetramethyl-0,0'-thiodi-p-phenylene phosphorothioate;
0,0,0',0'-tetraethyl S,S'-methylene bis-phosphorodithioate;
dimethyl 2-methoxycarbonyl-1-methylvinyl phosphate;
dimethyl 2,2-dichlorovinyl phosphate;
dimethyl-1,2-dibromo-2,2-dichloroethyl phosphate;
2,4-dinitro-6-(2-octyl)phenyl crotonate;
dimethyl 2-chloro-2-diethylcarbamoyl-1-methyl-vinyl phosphate;
N-methyl-1-naphthyl carbamate;
0,0-diethyl-S-(ethylthiomethyl)phosphorodithioate;
5 0,0-dimethyl-S-(ethylthiomethyl)phosphorodithioate;
0,0-dimethyl S-(4-oxobenzotriazine-3-methyl)phosphorodithioate;
2,3-p-dioxane S,S-bis(0,0-diethylphosphorodithioate);
10 0,0-diethyl O-(2-isopropyl-4-methyl-6-pyrimidinyl)phosphorothioate;
0,0-dimethyl S-(N-methylcarbamoylmethyl)phosphoro-
dithioate.

Formulations

As previously indicated, the diacylhydrazines and benzoic acid 1-alkyl, 2-alkyl and 2-cycloalkylhydrazides of this invention are excellent insect stomach poisons and have contact insecticidal activity. They are effective when applied to the foliage of plants which are to be protected from insect attack or when applied to the breeding grounds, food supply or habitat of insects. These diacylhydrazines are also highly effective systemic insecticidal agents when they are made available to the root systems of plants that are to be protected from insect attack. When used systematically, the active diacylhydrazines are applied to the soil or water in which the plants are growing, usually in the form of solid or liquid formulations which are readily dispersed and/or dissolved in said soil or water.

Emulsifiable concentrates, wet and dry flowable compositions, granular formulations, microemulsions and wettable powders all lend themselves to soil and/or water application and provide the desired insect control and requisite plant protection.

A typical emulsifiable concentrate formulation may be prepared by dispersing about 31% W/V of the diacylhydra-
zine such as 1-tert-butyl-1,2-bis(p-chlorobenzoyl)hydrazine; 1-tert-butyl-1,2-bis(3,4-dichlorobenzoyl)hydrazine or 1,2-dibenzoyl-1-tert-butylhydrazine 49% w/v of 2-pyrrolidone; in 10% w/v of n-butanol; 7% w/v of a polyalkylene glycol ether such as POLYFAR® S320 manufactured by Westvaco-Polychemicals, Charleston Heights, South Carolina and 3.0% w/v of nonylphenoxo polyethoxy ethanol offered by Rohm and Haas Co as TRITON® N101.

Emulsifiable concentrates are especially useful for distributing the active diacylhydrazines of this invention since they are readily dispersed in water for application as liquid sprays. They may also be added to irrigation water or flooded paddies such as used for rice cultivation, or they may be applied directly to the plants or the locus to be protected from insect infestation using aerial applicators or ground equipment designed for ultra low volume (ULV) or low volume (LV) application of the undiluted concentrates as finely divided discrete droplets.

Granular formulations may be prepared by dissolving the diacylhydrazine in a low-boiling solvent such as methylene chloride and spraying the thus prepared solution on a sorptive carrier such as kaolin, bentonite, attapulgite, montmorillonite or the like, in sufficient amount to provide from about 2% to 20% and preferably about 3% to 15% by weight, of active ingredient based on the total weight of the granulated product.

Wettable powder formulations can be prepared by grinding together about 30% to 75% by weight of the active diacylhydrazine with about 5% to 10% by weight of an anionic surfactant, such as a naphthalene sulfonate condensate or a sodium or ammonium salt of a condensed mono naphthalene sulfonic acid; about 3% to 5% by weight of an anionic surfactant such as an alkyl naphthalene sulfonate i.e. sodium di-n-butyl naphthalene sulfonate, sodium diisopropyl naphthalene sulfonate or the like and the remainder of the composition an inert diluent such as attapulgite, kaolin, montmorillonite, talc, diatomaceous earth or the like.
In practice, protection of living plants is achieved by applying to the foliage of said plants and/or to the soil, water or other media in which they are growing, about 0.1 kg/hectare to about 10.0 kg/hectare, preferably about 0.28 to 4.0 kg/hectare, of the formula (I) or formula (II) benzoic acid 2-alkyl- or 2-cycloalkylhydrazide. Advantageously, application of these formulations to the insects habitat, food supply and/or breeding grounds at the above said rates also provide control of insect populations in the treated area.

If the active formula (I) or formula (II) compound is applied as a dilute spray, said spray should contain 10 ppm to about 10,000 ppm of the active ingredient to provide the desired protection and insect control.

A typical emulsifiable concentrate formulation is prepared by dispersing about 30% w/v of the benzoic acid 1-alkyl-, 2-alkyl and 2-cycloalkylhydrazide of the invention in 50% w/v of 2-pyrrolidone; in 10% w/v of n-butanol; 7% w/v of a polyalkylene glycol ether, such as POLYFAR® S320 manufactured by Westvaco-Polychemicals, Charleston Heights, South Carolina; and 3.0% w/v of nonylphenoxy polyethoxy ethanol offered by Rohm and Haas Co as TRITON® N101.

Emulsifiable concentrates are especially useful for distributing the active benzoic acid 1-alkyl, 2-alkyl and 2-cycloalkylhydrazides of this invention since they are readily dispersed in water for application as liquid sprays. Such emulsifiable concentrates also may be added to irrigation water or flooded paddies, such as used for rice cultivation, or they may be applied directly to the plants or the locus to be protected from insect infestation using aerial applicators or ground equipment designed for ultra low volume (ULV) or low volume (LV) application of the undiluted concentrates as finely divided discrete droplets.

Granular formulations may be prepared by dissolving the active formula (I) or formula (II) hydrazide in a low-boiling solvent, such as methylene chloride, and spraying the thus-prepared solution on a sorptive carrier such as
kaolin, bentonite, attapulgite, montmorillonite or the like, in sufficient amount to provide from about 2% to 20%, preferably about 3% to 15%, by weight, of active ingredient based on the total weight of the granulated product.

Wettable powder formulations can be prepared by grinding together about 30% to 75% by weight of the active formula (I) or (II) hydrazide with about 5% to 10% by weight of an anionic surfactant, such as a naphthalene sulfonate condensate or a sodium or ammonium salt of a condensed mono naphthalene sulfonic acid; about 3% to 5% by weight of an anionic surfactant such as an alkyl naphthalene sulfonate, i.e. sodium di-n-butyl naphthalene sulfonate, sodium di-isopropyl naphthalene sulfonate or the like; and the remainder of the composition an inert diluent such as attapulgite, kaolin, montmorillonite, talc, diatomaceous earth or the like.

The following examples are presented herein simply as illustrations of the present invention and are not limitative thereof.

**EXAMPLE 1**
Preparation of benzoic acid, 2-tert-butylhydrazide
tert-Butylhydrazine hydrochloride (15.6 g, 0.125 mole) is dissolved in 350 mL of methylene chloride. To this solution is added 240 mL of 10% aqueous sodium hydroxide (24 g, 0.60 mole). A solution of benzoyl chloride (d = 1.211, 14.5 mL, 17.6 g, 0.125 mole) in methylene chloride is then added at moderate rate to the rapidly stirring two-phase system.

After stirring the mixture for 24 hours at ambient temperatures, the methylene chloride phase is removed, washed with 5% aqueous sodium hydroxide, water, saturated sodium chloride solution, and then dried over sodium sulfate. Evaporation in vacuo gives 19.3 g of white solid, mp 87-94°C, which is recrystallized from 2-propanol-water to give 13.0 g of product, mp 92-94°C.
Substituting p-chlorobenzoyl chloride for benzoyl chloride in the above reaction yields p-chlorobenzoic acid, 2-tert-butylhydrazide; melting point 116-122°C. Similarly, substituting p-fluorobenzoyl chloride, p-nitrobenzoyl chloride, o-toluyl chloride, m-fluorobenzoyl chloride, p-bromobenzoyl chloride, p-trifluoromethylbenzoyl chloride, o-anisyl chloride, p-toluyl chloride, o-chlorobenzoyl chloride, p-iodobenzoyl chloride, o-iodobenzoyl chloride, p-ethylbenzoyl chloride and o-fluorobenzoyl chloride, o-nitrobenzoyl chloride, for benzoyl chloride, yields respectively: p-fluorobenzoic acid, o-bromobenzoyl chloride, 2-tert-butylhydrazide; mp 136-138°C; p-nitrobenzoic acid, 2-tert-butylhydrazide; o-toluic acid, 2-tert-butylhydrazide; m-fluorobenzoic acid, 2-tert-butylhydrazide, mp 119-120°C; p-bromobenzoic acid, 2-tert-butylhydrazide; p-trifluoromethylbenzoic acid, 2-tert-butylhydrazide; anisic acid, 2-tert-butylhydrazide; p-toluic acid, 2-tert-butylhydrazide; o-chlorobenzoic acid, 2-tert-butylhydrazide; mp 68-70°C; o-iodobenzoic acid, 2-tert-butylhydrazide; p-ethylbenzoic acid, 2-tert-butylhydrazide; and o-fluorobenzoic acid, 2-tert-butylhydrazide; mp 58-59°C; o-nitrobenzoic acid, 2-tert-butylhydrazide; mp 116-118°C; o-bromobenzoic acid, 2-tert-butylhydrazide; mp 85-87°C; and N-methylanthranilic acid, 2-tert-butylhydrazide, mp 125-129°C.

The above reactions are illustrated below:

\[
\text{SeCO--} \text{RNH}_2 \text{Q} + \text{RNHNHR} + 10\% \text{NaOH}
\]

wherein Q is halogen, preferably chlorine; R is tert-butyl
or tert-amyl. Other compounds that can be prepared by the above procedure using the appropriately substituted benzoyl halide include: m-chlorobenzoic acid, 2-tert-butylhydrazide, mp 120-123°C; p-cyanobenzoic acid, 2-tert-butylhydrazide, mp 135-136°C; anthranilic acid, 2-tert-butylhydrazide, mp 165-167°C; tert-butyl or isopropyl; and X is hydrogen, halogen, C₁-C₃ alkyl, methoxy, methylamino, NH₂, nitro or CF₃.

**EXAMPLE 2**

**Preparation of 3,4-dichlorobenzoic acid, 2-tert-butylhydrazide**

Tert-butylhydrazine hydrochloride (12.4 g, 0.1 mole) is added to a solution of sodium carbonate (23.3 g, 0.22 mole) in 100 mL of water and 250 mL of ether. A solution of 3,4-dichlorobenzoyl chloride (20.9 g, 0.1 mole) in 50 mL of ether is then added dropwise at 0-15°C. After one hour, the reaction mixture is filtered and the filtrate is separated. The organic layer is washed with 100 mL of water, dried over anhydrous MgSO₄, filtered and evaporated. Recrystallization of the residue from 2-propanol gives white crystals: yield 6.4 g, mp 144-145°C.

Following the above procedure, but substituting 2,4-dichlorobenzoyl chloride or 2,6-dichlorobenzoyl chloride for 3,4-dichlorobenzoyl chloride, yields, respectively 2,4-dichlorobenzoic acid, 2-tert-butylhydrazide, mp 115-117°C and 2,6-dichlorobenzoic acid, 2-tert-butylhydrazide, mp 173-174°C.

Similarly, substituting 2-chloro-4-nitrobenzoyl chloride, 3-bromo-4-methylbenzoyl chloride, 2,6-difluorobenzoyl chloride, 2,5-dichlorobenzoyl chloride, 3,5-dichlorobenzoyl chloride or naphthoyl chloride, for 3,4-dichlorobenzoyl chloride, yields respectively: 2-chloro-4-nitrobenzoic acid, 2-(tert)-butylhydrazide; 3-bromo-4-methylbenzoic acid, 2-(tert)-butylhydrazide; mp 95-97°C; 2,5-dichlorobenzoic acid, 2-(tert)-butylhydrazide and 3,5-
dichlorobenzoic acid, 2-(tert)-butylhydrazide, mp 163-165°C; 1-naphthoic acid, 2-(tert)-butylhydrazide mp 148-150°C.

These reactions are illustrated below:

\[
\text{(CH}_3\text{)}_3\text{CNHNH}_2\text{.HCl} + \text{CO-Q} + \text{Na}_2\text{CO}_3 \xrightarrow{\text{H}_2\text{O/Ether}} \text{\begin{center} CO-NHNHC(CH}_3\text{)}_3\end{center}}
\]

wherein Q is halogen, preferably chlorine; X and Y are each independently halogen, C\(_1\)-C\(_3\) alkyl, methoxy, nitro or CF\(_3\) and when taken together XY may represent \[\text{\begin{center} \end{center}}\].

**EXAMPLE 3**

**Preparation of 1,2-dibenzoyl-1-tert-butylhydrazine**

t-Butylhydrazine hydrochloride (101 g, 0.81 mole) is dissolved in 970 mL of 10% sodium hydroxide (97 g, 2.4 mole) in a three-liter flask with mechanical stirring. After addition of one liter of ether, the flask is fitted with a condenser and addition funnel.

Benzoyl chloride (176 mL, 213 g, 1.52 mole) in 70 mL of ether is then added over about a one hour period. The reaction proceeds exothermically with formation of a white solid. After stirring overnight, the mixture is filtered and the resulting solids dried and then recrystallized from isopropyl alcohol. White crystals are collected and dried and weighed to give 147.0 g of product, mp 174-176°C.

Substituting 2,6-difluorobenzoyl chloride, 4-ethylbenzoyl chloride, 4-nitrobenzoyl chloride, 4-iodobenzoyl
chloride, 2-chloro-4-nitrobenzoyl chloride, 3-bromo-4-
toluoyl chloride, 2,5-dichlorobenzoyl chloride or 3,4-
(methylenedioxy) benzoyl chloride or 3,4-naphthoyl chloride
or benzoyl chloride in the above reaction yields, respect-
tively. l-tert-butyl-1,2-bis(2,6-difluorobenzoyl)hydra-
zine, mp 193-194°C; l-tert-butyl-1,2-bis (p-ethylbenzoyl)-
hydrazine, mp 178°C; l-tert-butyl-1,2-bis (p-nitroben-
zoyl)hydrazine, mp >240°C; l-tert-butyl-1,2-bis (p-iodo-
benzoyl)hydrazine, mp >230°C; l-tert-butyl-1,2-bis(2-
chloro-4-nitrobenzoyl)hydrazine, mp 155-158°C; l-tert-
butyl-1,2-bis(3-bromo-p-toluoyl)hydrazine, mp 177-178°C;
l-tert-butyl-1,2-bis(2,5-dichlorobenzoyl)hydrazine,
mp 198-200°C; l-tert-butyl-1,2-bis[3,4-(methylenedioxy)-
benzoyl]hydrazine, mp >235°C; and l-tert-butyl-1,2-di-2-
naphthoylhydrazine, 235.

These reactions are illustrated below:

\[
\text{CO-Q} + (\text{CH}_3)_3\text{CNHH}_2\cdot\text{HCl} + \text{NaOH}
\]

\[
\text{CO-NH-N--x}
\]

\[
\text{C(CH}_3)_3
\]

wherein Q is halogen, preferably chlorine and X and Y are
each independently hydrogen, halogen, C\textsubscript{1}-C\textsubscript{3} alkyl, methoxy, nitro, CF\textsubscript{3} or R\textsubscript{1}CF\textsubscript{2}Z and when taken together X and Y may form
a ring in which XY are represented by the structure -OCH\textsubscript{2}O,
-OCF\textsubscript{2}O or Z is S or O; R\textsubscript{1} is H, F, CHF\textsubscript{2} or CF\textsubscript{3}. 
EXAMPLE 4

Preparation of 2-benzoyl-1-tert-butyl-1-(3,4-dichlorobenzoyl)hydrazine

Benzoyl-2-tert-butylhydrazine (4.8 g, 0.025 mole) is stirred vigorously in a two-phase system of 50 mL of methylene chloride and 25 mL of 10% aqueous sodium hydroxide (2.5 g, 0.063 mol) until all dissolves. To this solution is added a solution of 3,4-dichlorobenzoyl chloride (7.3 g, 0.025 mol) in methylene chloride. After stirring the two-phase mixture several hours at ambient temperature, the solid is removed and washed with water and methylene chloride. Recrystallization from 2-propanol gives 7.1 g (78%) of product with mp 234-235.5°C.

The reactions may be graphically illustrated as follows:

\[ \text{CO-NH-NH} + \text{CO} \xrightarrow{\text{10\% NaOH}} \]

EXML

Example 5

Preparation of 1-benzoyl-1-tert-butyl-2-(3,4-dichlorobenzoyl)hydrazine

3,4-Dichlorobenzoyl-2-tert-butylhydrazine (5.63 g, 0.0215 mole) is added to a rapidly stirring mixture of 40 mL of methylene chloride and 20 mL of 10% aqueous sodium hydroxide (2 g, 0.05 mole). Benzoyl chloride (d = 1.211, 2.5 mL, 3.03 g, 0.0215 mole) in methylene chloride is added
and the reaction mixture stirred vigorously for approximately three hours at ambient temperature. The resulting solid is collected and washed with water and methylene chloride.

The dried product weighs 6.18 g with mp 206.5-208.5°C.

The reaction is illustrated below:

Following the above procedure but substituting the appropriately substituted benzoyl-2-tert-butylhydrazine for 3,4-dichlorobenzoyl-2-tert-butylhydrazine and the appropriately substituted benzoyl chloride for benzoyl chloride yields the following compounds: 1-tert-butyl-2-(p-chlorobenzoyl)-1-p-toluoylhydrazine, mp 223.5-224.0°C; 1-p-anisoyl-1-tert-butyl-2-(3,4-dichlorobenzoyl)hydrazine, mp >230°C; 1-tert-butyl-2-(3,4-dichlorobenzoyl)-1-o-toluoylhydrazine, mp 133-136°C; 1-tert-butyl-2-(3,4-dichlorobenzoyl)-1-(p-nitrobenzoyl)hydrazine, mp >230°C; 1-tert-butyl-2-(3,4-dichlorobenzoyl)-1-(α,α,α-trifluoro-p-toluoyl)hydrazine, mp 212-213°C; and 1-tert-butyl-2-(3,4-dichlorobenzoyl)-1-(α,α,α-trifluoro-o-toluoyl)hydrazine, mp 171-172.5°C.

**EXAMPLE 6**

Preparation of benzoic acid, 3,4-dichloroisopropylidenehydrazine

3,4-Dichlorobenzoic acid hydrazide (11.7 g, 0.060 mole) is placed in the thimble of a Soxhlet extractor
and flooded with hot acetone from an attached distillation flask. After overnight reflux, the acetone mixture concentrated under vacuum to afford a white solid. Recrystallization from ethyl acetate petroleum ether gives 9.5 g of the title compound as white crystals, mp 141-144°C.

This reaction is illustrated as below:

Following the above procedure but substituting the appropriate aldehyde or ketone for acetone yields the following compounds: benzoic acid (1-ethylpropylidene)hydrazide, mp 89-91°C; and benzoic acid (2,2-dimethylpropylidene)hydrazide, mp 168-169°C.

**EXAMPLE 7**

**Preparation of 3,4-dichlorobenzoic acid, 2-isopropylhydrazide**

3,4-Dichlorobenzoic acid isopropylidenehydrazide (9.2 g, 0.040 mole) and 100 mg of platinum oxide in 100 mL of methanol in a Parr hydrogenation apparatus is shaken for one hour and 30 minutes under an initial hydrogen pressure of 40 psig. The filtered reaction mixture is concentrated under vacuum and the resulting solids are recrystallized three times from isopropyl alcohol to give 2.6 g of the title compound as a white crystalline product, mp 112.5-115°C.

The reaction is illustrated below:
EXAMPLE 8
Preparation of L-benzoyl-2-(3,4-dichlorobenzoyl)-L-isopropylhydrazine

A mixture of 3,4-dichlorobenzoic acid, 2-isopropylhydrazide (0.98 g, 0.004 mole) and benzoyl chloride (0.56 g, 0.004 mole) is stirred overnight in 1.2 mL of ethylene dichloride and 6.5 mL of 10% sodium hydroxide. The organic phase is removed and the aqueous mixture is extracted with 25 mL of ethylene dichloride. The organic extracts are combined and concentrated to a yellow oil which is taken up in hot isopropyl alcohol. Cooling the alcohol solution causes precipitation of the title compound as a white crystalline product, which is collected by filtration and has a mp of 157°C.

Following one or more of the procedures described in examples 1-8 above yields the compounds listed in Table I below. The reactions is graphically illustrated below.
### TABLE I
Compounds having the structure

![Chemical structure diagram](image)

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>Y</th>
<th>M</th>
<th>N</th>
<th>Bp°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4Cl</td>
<td>H</td>
<td>4Cl</td>
<td>&gt;240</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>3Cl</td>
<td>4Cl</td>
<td>228.0 - 229.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2CH₃</td>
<td>H</td>
<td>2CH₃</td>
<td>H</td>
<td>196.0 - 197.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2Cl</td>
<td>4Cl</td>
<td>2Cl</td>
<td>4Cl</td>
<td>115.0 - 117.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4CF₃</td>
<td>H</td>
<td>4CF₃</td>
<td>226.0 - 227.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4OCH₃</td>
<td>H</td>
<td>4OCH₃</td>
<td>119.0 - 201.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>H</td>
<td>4Cl</td>
<td>206.5 - 208.5</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>H</td>
<td>4CN</td>
<td>&gt;240</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>H</td>
<td>4OCH₃</td>
<td>&gt;230</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>-CH=CH-CH=CH- (2,3)</td>
<td>-CH=CH-CH=CH- (2,3)</td>
<td>182.0 - 183.0</td>
<td>α-naphthyl</td>
<td></td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>2CH₃</td>
<td>H</td>
<td>133.0 - 136.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>H</td>
<td>SO₂CH₃</td>
<td>237.0 - 240.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>3Cl</td>
<td>4Cl</td>
<td>154.0 - 156.0</td>
</tr>
<tr>
<td>C(CH₃)₂</td>
<td>4Br</td>
<td>H</td>
<td>4Br</td>
<td>H</td>
<td>219.0 - 220.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4F</td>
<td>H</td>
<td>4F</td>
<td>196.0 - 198.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>H</td>
<td>4NO₂</td>
<td>&gt;230</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>H</td>
<td>4CF₃</td>
<td>212.0 - 213.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>H</td>
<td>4CH₃</td>
<td>225.5 - 227.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>3Cl</td>
<td>4Cl</td>
<td>234.0 - 235.5</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>2F</td>
<td>6F</td>
<td>195.0 - 197.0</td>
</tr>
<tr>
<td>C(CH₃)₂</td>
<td>3Cl</td>
<td>4Cl</td>
<td>H</td>
<td>H</td>
<td>163.0 - 164.5</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4CH₃</td>
<td>H</td>
<td>4CH₃</td>
<td>218.0 - 219.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4Cl</td>
<td>3Cl</td>
<td>4Cl</td>
<td>190.0 - 192.0</td>
</tr>
<tr>
<td>R</td>
<td>X</td>
<td>Y</td>
<td>M</td>
<td>N</td>
<td>Tp°C</td>
</tr>
<tr>
<td>------------</td>
<td>------</td>
<td>------</td>
<td>-------</td>
<td>-------</td>
<td>--------</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>2F</td>
<td>H</td>
<td>2F</td>
<td>H</td>
<td>135.0 - 137.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>2CF₃</td>
<td>H</td>
<td>171.0 - 172.5</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>3Cl</td>
<td>H</td>
<td>3Cl</td>
<td>H</td>
<td>205.0 - 206.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>H</td>
<td>2Cl</td>
<td>H</td>
<td>2Cl</td>
<td>222.0 - 223.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>2F</td>
<td>6F</td>
<td>2F</td>
<td>6F</td>
<td>236.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>-OCH₂O-(3,4)</td>
<td>-OCH₂O-(3,4)</td>
<td>220.0 - 221.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>2Cl</td>
<td>4NO₂</td>
<td>2Cl</td>
<td>4NO₂</td>
<td>155.0 - 158.0</td>
</tr>
<tr>
<td>CH(CH₃)₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>199.0 - 201.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>3Cl</td>
<td>5Cl</td>
<td>3Cl</td>
<td>5Cl</td>
<td>219.0 - 221.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>H</td>
<td>2CF₃</td>
<td>H</td>
<td>2CF₃</td>
<td>211.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>H</td>
<td>3CH₃</td>
<td>H</td>
<td>3CH₃</td>
<td>152.0 - 153.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>5Cl</td>
<td>5Cl</td>
<td>5Cl</td>
<td>5Cl</td>
<td>198.0 - 199.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>4OC₂H₅</td>
<td>H</td>
<td>4OC₂H₅</td>
<td>H</td>
<td>187.0 - 188.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>4SC₃H₃</td>
<td>H</td>
<td>4SC₃H₃</td>
<td>H</td>
<td>197.0 - 200.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>4C₂H₅</td>
<td>H</td>
<td>4C₂H₅</td>
<td>H</td>
<td>177.5</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>3Br</td>
<td>4CH₃</td>
<td>3Br</td>
<td>4CH₃</td>
<td>177.0 - 177.5</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>2I</td>
<td>H</td>
<td>2I</td>
<td>H</td>
<td>206.0 - 207.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>4I</td>
<td>H</td>
<td>4I</td>
<td>H</td>
<td>&gt;230.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>4NO₂</td>
<td>H</td>
<td>4NO₂</td>
<td>H</td>
<td>&gt;240.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>4OCF₂CHF₂</td>
<td>H</td>
<td>4OCF₂CHF₂</td>
<td>H</td>
<td>199.0 - 200.0</td>
</tr>
<tr>
<td>(CH₃)₃</td>
<td>2Br</td>
<td>H</td>
<td>2Br</td>
<td>H</td>
<td>218.0 - 219.0</td>
</tr>
<tr>
<td>R</td>
<td>X</td>
<td>Y</td>
<td>M</td>
<td>N</td>
<td>mp°C</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3F</td>
<td>H</td>
<td>3F</td>
<td>H</td>
<td>173.0 - 175.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2CO-0CH₃</td>
<td>H</td>
<td>2CO-0CH₃</td>
<td>H</td>
<td>173.0 - 175.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3F</td>
<td>5F</td>
<td>3F</td>
<td>5F</td>
<td>165.0 - 169.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2F</td>
<td>4F</td>
<td>2F</td>
<td>4F</td>
<td>165.0 - 166.5</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>H</td>
<td>4Cl</td>
<td>&gt;240</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>4Cl</td>
<td>2CH₃</td>
<td>4Cl</td>
<td>166.5 - 169.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>4Cl</td>
<td>210.0 - 212.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>4Cl</td>
<td>223.5 - 224.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>4Cl</td>
<td>194.0 - 195.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2Cl</td>
<td>H</td>
<td>3Cl</td>
<td>H</td>
<td>&gt;250</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2Cl</td>
<td>H</td>
<td>183.0 - 185.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>H</td>
<td>H</td>
<td>3Cl</td>
<td>187.0 - 189.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4Cl</td>
<td>H</td>
<td>H</td>
<td>194.0 - 195.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2Cl</td>
<td>H</td>
<td>4Cl</td>
<td>H</td>
<td>150.0 - 153.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4Cl</td>
<td>2Cl</td>
<td>H</td>
<td>198.0 - 199.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2Cl</td>
<td>H</td>
<td>4Cl</td>
<td>H</td>
<td>225.0 - 226.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>H</td>
<td>2Cl</td>
<td>H</td>
<td>266.0 - 270.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4Cl</td>
<td>3Cl</td>
<td>H</td>
<td>142.5 - 145.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2Cl</td>
<td>H</td>
<td>2Cl</td>
<td>H</td>
<td>186.0 - 189.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4Cl</td>
<td>2Cl</td>
<td>H</td>
<td>196.0 - 198.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>H</td>
<td>H</td>
<td>3Cl</td>
<td>213.0 - 216.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2NO₂</td>
<td>H</td>
<td>3Cl</td>
<td>H</td>
<td>233.5 - 234.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>3Cl</td>
<td>H</td>
<td>H</td>
<td>4Cl</td>
<td>217.0 - 219.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2NH₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>212.0 - 213.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>3,4-0CH₂O-</td>
<td>H</td>
<td>213.0 - 214.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>3F</td>
<td>H</td>
<td>3Cl</td>
<td>206.0 - 207.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2NO₂</td>
<td>H</td>
<td>165.0 - 172.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4F</td>
<td>H</td>
<td>3Cl</td>
<td>200.0 - 203.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>196.0 - 198.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2NO₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>152.0 - 155.0</td>
</tr>
</tbody>
</table>
### TABLE I (Continued)

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>Y</th>
<th>M</th>
<th>N</th>
<th>mp°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(CH₃)₃</td>
<td>-2,3-</td>
<td></td>
<td>H</td>
<td>H</td>
<td>175.0 - 178.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2F</td>
<td>H</td>
<td>175.0 - 177.0</td>
</tr>
<tr>
<td>5 C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2OCH₃</td>
<td>H</td>
<td>152.0 - 154.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2CH₃</td>
<td>H</td>
<td>206.0 - 209.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2F</td>
<td>H</td>
<td>2NO₂</td>
<td>H</td>
<td>190.0 - 194.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4F</td>
<td>2F</td>
<td>H</td>
<td>157.0 - 159.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4Cl</td>
<td>H</td>
<td>4F</td>
<td>213.0 - 232.0</td>
</tr>
<tr>
<td>10 C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>3NO₂</td>
<td>213.0 - 217.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2Cl</td>
<td>4Cl</td>
<td>H</td>
<td>4F</td>
<td>237.0 - 240.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2Cl</td>
<td>4Cl</td>
<td>H</td>
<td>3Cl</td>
<td>236.0 - 240.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>4Cl</td>
<td>H</td>
<td>4F</td>
<td>231.0 - 232.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2Br</td>
<td>H</td>
<td>184.0 - 187.0</td>
</tr>
<tr>
<td>15 C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>4Br</td>
<td>224.0 - 227.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2F</td>
<td>6F</td>
<td>189.0 - 190.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2NO₂</td>
<td>H</td>
<td>H</td>
<td>4F</td>
<td>153.0 - 156.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>-2,3-</td>
<td></td>
<td>240.0 - 242.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2Cl</td>
<td>4NO₂</td>
<td>199.0 - 201.0</td>
</tr>
<tr>
<td>20 CH₂CH(CH₃)₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>168.0 - 169.0</td>
</tr>
<tr>
<td>CH(CH₃)(C₂H₅)</td>
<td>N</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>168.0 - 170.0</td>
</tr>
<tr>
<td>n-C₃H₇</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>126.0 - 127.0</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>121.0 - 124.0</td>
</tr>
<tr>
<td>C(CH₃)₂C₂H₅</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>158.0 - 160.0</td>
</tr>
<tr>
<td>25 C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>4OCH₃</td>
<td>217.0 - 218.4</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2I</td>
<td>H</td>
<td>175.0 - 177.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>3OCH₃</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLE I (Continued)

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>Y</th>
<th>N</th>
<th>M</th>
<th>mp°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2CN</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>20C₂H₅</td>
<td>H</td>
<td>168.0-169.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2CF₃</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2SCH₃</td>
<td>H</td>
<td>190.0-192.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2SO₂CH₃</td>
<td>H</td>
<td>144.0-144.5</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2Cl</td>
<td>4Cl</td>
<td>136.0-138.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>20CH₃</td>
<td>6OCH₃</td>
<td>175.0-176.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2F</td>
<td>4Cl</td>
<td>2F</td>
<td>4Cl</td>
<td>154.0-155.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2I</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>223.0-224.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>3F</td>
<td>H</td>
<td>173.0-174.0</td>
</tr>
<tr>
<td>CH(CH₃)₂</td>
<td>H</td>
<td>H</td>
<td>4F</td>
<td>H</td>
<td>184.0-185.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2NO₂</td>
<td>4Cl</td>
<td>129.0-131.0</td>
</tr>
<tr>
<td>C(CH₃)₂C₂H₅</td>
<td>H</td>
<td>2F</td>
<td>H</td>
<td>2F</td>
<td>123.0-126.0</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>4SCF₂CHF₂</td>
<td>H</td>
<td>4SCF₂OCHF₂</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>4S(O)CF₂</td>
<td>H</td>
<td>4S(O)CF₂</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CHF₂</td>
<td>OCHF₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4S(O)₂CF₂</td>
<td>H</td>
<td>4S(O)₂CF₂</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CHF₂</td>
<td>OCHF₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>2OCF₃</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>4Cl</td>
<td>H</td>
<td>2OCHF₂</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>H</td>
<td>H</td>
<td>2SCF₃</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>4F</td>
<td>H</td>
<td>2S(O)CF₃</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
EXAMPLE 9
Preparation of acetone tert-butylhydrazone

To 6.6 g of acetone, cooled in an ice bath, is added 5.0 g of tert-butylhydrazine. The mixture is stirred and then allowed to stand for several minutes. Ether and potassium hydroxide pellets are then added to the mixture. The mixture is stirred, and then the ethereal layer is separated from the mixture. Distillation of the ethereal layer yields the product acetone tert-butylhydrazone b.p. 132-134°C.

The reaction is illustrated as follows:

\[
(CH_3)_3C-N\equiv NH_2 + CH_3-C\equiv CH_3 \rightarrow (CH_3)_3C-N\equiv N\equiv C(CH_3)_2
\]

EXAMPLE 10
Preparation of 1-tert-butyl-2-isopropylidenehydrazide of benzoic acid

Acetone tert-butylhydrazone (2.0 g) is admixed with 4.4 g of benzoyl chloride and 15 mL of 10% sodium hydroxide. The mixture is stirred until the benzoyl chloride odor is no longer detectable. The resulting product is then dissolved in ether and dried over magnesium sulfate. Evaporation of the solvent from the mixture leaves acetone N-tert-butyl-N-benzoylhydrazone, b.p. 100-103°C. This product also is referred to as 1-tert-butyl-2-isopropylidenehydrazide of benzoic acid.

Following the above procedure, but substituting p-chlorobenzoyl chloride for benzoyl chloride yields the product 1-tert-butyl-2-isopropylidenehydrazide of p-chlorobenzoic acid.

Substitution of the o-nitrobenzoyl chloride or o-fluorobenzoyl chloride for benzoyl chloride in the above
procedure yields, respectively, 1-tert-butyl-2-isopropylidenehydrazide of o-nitrobenzoic acid and 1-tert-butyl-2-isopropylidenehydrazide of p-fluorobenzoic acid. The reactions are illustrated as follows:

\[ \text{CH}_3\text{C}_3\text{N-N=CH}_3 + \text{C-C-Cl} \]

\[ \text{C-CN-N=C(CH}_3)_2 \]

**EXAMPLE 11**

**Preparation of benzoic acid, 1-tert-butylhydrazide**

A solution of 0.5 g of the 1-tert-butyl-2-isopropylidenehydrazide of benzoic acid, 3 mL of 10% hydrochloric acid and 3 mL of methanol is mixed and allowed to stand for 12 hours. The mixture is made basic with dilute sodium hydroxide. The methanol is evaporated from the mixture yielding the product 1-tert-butylhydrazide of benzoic acid, m.p. 117-123°C.

The above procedure is used, but 1-tert-butyl-2-isopropylidenehydrazide of p-chlorobenzoic acid is substituted for 1-tert-butyl-2-isopropylidenehydrazide of benzoic acid. This yields 1-tert-butylhydrazide of p-chlorobenzoic acid, m.p. 134-136°C.

Similarly, 1-tert-butylhydrazide of o-nitrobenzoic acid, m.p. 141-144°C and 1-tert-butylhydrazide of p-fluorobenzoic acid, m.p. 136-137°C; is prepared by the above reaction using the appropriately substituted benzoic acid,
l-tert-butyl-2-isopropylidenehydrazide. The reactions are illustrated as follows:

\[
\begin{align*}
\text{N} & \quad \text{N} = \text{C} \left( \text{CH}_3 \right) \left( \text{CH}_3 \right) \\
\text{C} \left( \text{CH}_3 \right) & \quad \text{X} \quad \text{Y} \\
\text{N} & \quad \text{N} = \text{C} \left( \text{CH}_3 \right) \left( \text{CH}_3 \right) \\
\text{C} \left( \text{CH}_3 \right) & \quad \text{X} \quad \text{Y}
\end{align*}
\]

5 **Insecticidal activity of the compounds of the invention**

The compounds of the present invention exhibit insecticidal activity against a variety of insects at various concentrations of active ingredient in acetone-water solutions. As illustrative of this insecticidal activity is control of *Spodoptera eridania* (third-instar larvae, southern armyworm), *Spodoptera eridania* (seven-day residual), *Spodoptera eridania* (third-instar cut-stem systemic test, southern armyworm), *Anopheles quadrinaculatus* (adults, common malaria mosquito); *Heliothis virescens* (third-instar tobacco budworm), *Blattella germanica* (residue test, adult male German cockroach), and *Leptinotarsa decemlineata* (Colorado potato beetles).

Further, systemic activity of the compounds is observed when tested for controlling Colorado potato beetles (*Leptinotarsa decemlineata*) on potato plants, (*Solanum tuberosum*). These beetles are resistant to carbamates, phosphates and pyrethroids but are controlled by the present compounds.

Bean plants, *Phaseolus limensis*, also are protected from southern armyworms, *Spodoptera eridania* and systemically protected from potato leafhoppers, *Empoasca abrupta*. 
Maize plants (Zea mays L. plants) also are protected from insect attack of southern armyworm larvae (Spodoptera eridania, third-instar larvae, southern armyworm) and systemically from southern corn rootworm (Diabrotica undecim-punctata howardi).

Rice plants, Oryza sativa, are protected via systemic application, as well as by foliar application, from armyworms, Spodoptera frugiperda, and leafhoppers, Empoasca abrupta.

Cotton plants Gossypium hirsutum, also are systemically protected, as well as by foliar application from tobacco budworms (Heliotris virescens).
WHAT IS CLAIMED IS:

The claims defining the invention are as follows:

1. A compound having the structural formula,

   ![Structural Formula]

   wherein R is C₂-C₆ alkyl; X, Y, M and N are each independently H, C₁-C₃ alkyl, C₁-C₃ alkoxy, C₁-C₃ alkylthio, C₁-C₃ alkylsulfinyl, C₁-C₃ alkylsulfonyl, cyano, F, Cl, Br, I, nitro, CF₃, R₁CF₂Z⁻, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N, and when taken together, X and Y may form a ring in which XY are represented by the structure,

   ![Ring Structure]

   and when taken together, M and N may form a ring in which MN are represented by the structure,

   ![Ring Structure]

   Z is S(O)n or O; R₁ is H, F, CHF₂, CHFCl or CF₃; R₂ is C₁-C₃ alkyl, C₁-C₃ alkoxy or R₃R₄N; R₃ is H or C₁-C₃ alkyl; R₄ is H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2; with the provisos that at least one of X, Y, M or N is a substituent other than hydrogen and when M is para-nitro, at least one other of X, Y, or N must be a substituent other than hydrogen.
2. A compound according to Claim 1, wherein R is \(-C(CH_3)_3, C(CH_3)_2C_2H_5\) or \(CH(CH_3)_2\); and X, Y, M and N is a substituent other than hydrogen.

3. A compound according to Claim 1, wherein R is isopropyl, tert-butyl, or tert-amyl; X, Y, M and N are each independently H, C\(_1\) - C\(_3\) alkyl, F, Cl, Br, I, or nitro with the provisos that at least one of X, Y, M or N is a substituent other than hydrogen and when M is para-nitro, at least one of X, Y, or N must be a substituent other than hydrogen.

4. A compound according to Claim 1, wherein said compound is 1-tert-butyl-1,2-bis(3,4-dichlorobenzoyl)hydrazine; wherein said compound is 1-tert-butyl-1,2-bis(p-chlorobenzoyl)hydrazine; wherein said compound is 2-benzoyl-1-tert-butyl-1-(m-chlorobenzoyl)hydrazine; wherein said compound is 1-tert-butyl-1,2-bis(p-fluorobenzoyl)hydrazine; wherein said compound is 2-benzoyl-1-tert-butyl-1-(o-nitrobenzoyl)hydrazine; wherein said compound is 2-benzoyl-1-tert-butyl-1-(o-nitrobenzoyl)hydrazine.

5. A method for controlling insects, said method characterizing: contacting said insects, their habitat, breeding grounds or feed with an insecticidally-effective amount of a compound of the formula,

\[
\text{R} \quad \text{X} \quad \text{N} \quad \text{N} \quad \text{M} \quad \text{O}
\]

wherein R is C\(_2\) - C\(_6\) alkyl; X, Y, M and N are each independently H, C\(_1\) - C\(_3\) alkyl, C\(_1\) - C\(_3\) alkoxy, C\(_1\) - C\(_3\) alkylthio, C\(_1\) - C\(_3\) alkylsulfanyl, C\(_1\) - C\(_3\) alkylsulfonyl, cyano, F, Cl, Br, I,
nitro, CF₃, R₁CF₂Z-, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N, and when taken together, X and Y may form a ring in which XY are represented by the structure,

-OC₂H₂-, -OCF₂- or \( \text{structure} \);

and when taken together, M and N may form a ring in which MN are represented by the structure,

-OC₂H₂-, -OCF₂- or \( \text{structure} \);

Z is S(O)n or O; R₁ is H, F, CHF₂, CHFCl or CF₃; R₂ is C₁-C₃ alkyl, C₁-C₃ alkoxy, or R₃R₄N; R₃ is H or C₁-C₃ alkyl; R₄ is H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2.

6. A method according to Claim 5, wherein said compound is,

[Chemical structure diagram]

wherein R is C(CH₃)₃, CH(CH₃)₂ or C(CH₃)₂C₂H₅.

7. A method according to Claim 6, wherein said compound is 1-tert-butyl-1,2-bis(3,4-dichlorobenzoyl)hydrazine; wherein said compound is 1-tert-butyl-1,2-bis(p-chlorobenzoyl)hydrazine; wherein said compound is 1,2-dibenzoyl-1-tert-butylhydrazine; wherein said compound
is 2-benzoyl-1-tert-butyl-l-(m-chlorobenzoyl)hydrazine; wherein said compound is 1-tert-butyl-1,2-bis(p-fluorobenzoyl)hydrazine.

8. An insecticidal composition characterizing: a compound of the formula,

![Chemical Structure]

wherein R is C2-C6 alkyl; X, Y, M and N are each independently H, C1-C3 alkyl, C1-C3 alkoxy, C1-C3 alkylthio, C1-C3 alkylsulfinyl, C1-C3 alkylsulfonyl, cyano, F, Cl, Br, I, nitro, CF3, R1CF2Z-, 1,1-difluoro-2,2-dichloroethoxy, R2CO or R3R4N, and when taken together, X and Y may form a ring in which XY are represented by the structure,

-0CH2O-, -OCF20- or [Diagram]

and when taken together, M and N may form a ring in which MN are represented by the structure,

-0CH2O-, -OCF20- or [Diagram]

Z is S(0)n or O; R1 is H, F, CHF2, CHFCl or CF3; R2 is C1-C3 alkyl, C1-C3 alkoxy or R3R4N; R3 is H or C1-C3 alkyl; R4 is
H, C₁⁻C₃ alkyl or R₅CO; R₅ is H or C₁⁻C₃ alkyl and n is 0, 1 or 2.

9. A method of systemically protecting a living plant through an extended period of active growth from insects which infest said growing plants, said method characterizing: applying to the soil or other media in which it is growing, a systemically-effective amount of a compound having the formula,

\[
\begin{align*}
\text{R} & \quad \text{N} \\
\text{X} & \quad \text{Y} \\
\text{M} & \quad \text{N}
\end{align*}
\]

wherein R is C₂⁻C₆ alkyl; X, Y, M and N are each independently H, C₁⁻C₃ alkyl, C₁⁻C₃ alkoxy, C₁⁻C₃ alkylthio, C₁⁻C₃ alkylsulfinyl, C₁⁻C₃ alkylsulfonyl, cyano, F, Cl, Br, I, nitro, CF₃, R₁CF₂Z⁻, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N, and when taken together, X and Y may form a ring in which XY are represented by the structure,

\[
\begin{array}{c}
-\text{OCH₂O}^- \\
-\text{OCF₂O}^-
\end{array}
\]

and when taken together, M and N may form a ring in which MN are represented by the structure,

\[
\begin{array}{c}
-\text{OCH₂O}^- \\
-\text{OCF₂O}^-
\end{array}
\]

Z is S(0)n or O; R₁ is H, F, CH₂, CHFCl or CF₃; R₂ is C₁⁻C₃ alkyl, C₁⁻C₃ alkoxy or R₃R₄N; R₃ is H or C₁⁻C₃ alkyl; R₄ is
H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2.

10. A method according to Claim 9, wherein said systemically-effective compound is applied to soil in which they are growing at a rate of about 0.01 kg/hectare to about 10.0 kg/hectare.

11. A method according to Claim 10, wherein said compound is 1,2-dibenzoyl-1-tert-butylhydrazine.

12. A compound having the structural formula:

\[
\text{(II)}
\]

wherein R and R₆ are each independently hydrogen, C₂-C₆ alkyl or C₅-C₆ cycloalkyl; X and Y are each independently H, C₁-C₃ alkyl, C₁-C₃ alkoxy, C₁-C₃ alkylthio, C₁-C₃ alkylsulfinyl, C₁-C₃ alkylsulfonyl, cyano, F, Cl, Br, nitro, CF₃, R₁CF₂Z, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N and when taken together X and Y may form a ring in which XY are represented by the structure,

\[
\text{-OC₂H₅-}, \text{-OCF₂O-} \text{ or } \text{ }
\]

Z is S(0)n or 0; R₁ is H, F, CHF₂, CHFCl or CF₃; R₂ is C₁-C₃ alkyl, C₁-C₃ alkoxy or R₃R₄N; R₃ is H or C₁-C₃ alkyl; R₄ is H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2; with the provisos that when R is hydrogen, R₆ is C₂-C₅ alkyl or C₅-C₆ cycloalkyl and when R₆ is hydrogen, R is C₂-C₅.
alkyl or C₅-C₆ cycloalkyl; and provided also that when R is tert-butyl and Y is chloro in the para position of the ring, X is a substituent other than hydrogen.

13. A compound according to Claim 12, wherein R is tert-butyl and R₆ is hydrogen.

14. A compound according to Claim 13, wherein R is hydrogen and R₆ is tert-butyl.

15. A compound according to Claim 12, wherein said compound is 2,6-dichlorobenzoic acid, 2-tert-butylhydrazide; wherein said compound is 2,6-difluorobenzoic acid, 2-tert-butylhydrazide; wherein said compound is o-chlorobenzoic acid, 2-tert-butylhydrazide; wherein said compound is o-fluorobenzoic acid, 2-tert-butylhydrazide; wherein said compound is o-toluic acid, 2-tert-butylhydrazide; wherein said compound is o-iodobenzoic acid, 2-tert-butylhydrazide; wherein said compound is l-naphthoic acid, 2-tert-butylhydrazide; wherein said compound is 2,4-dichlorobenzoic acid, 2-tert-butylhydrazide; wherein said compound is o-anisic acid, 2-tert-butylhydrazide; wherein said compound is p-fluorobenzoic acid 1-tert-butylhydrazide; wherein said compound is benzoic acid, 1-tert-butylhydrazide.

16. An insecticidal composition characterizing: an insecticidally-effective amount of a compound of the formula,

\[
\begin{align*}
&\text{CO} \quad \text{N} \quad \text{NH} \quad \text{R} \\
&X \quad Y \quad R_6
\end{align*}
\]

wherein R and R₆ are each independently hydrogen, C₂-C₆ alkyl or C₅-C₆ cycloalkyl; X and Y are each independently H, C₁-C₃ alkyl, C₁-C₃ alkoxy, C₁-C₃ alkylthio, C₁-C₃ alkyl-
sulfinyl, C₁-C₃ alkylsulfonyl, cyano, F, Cl, Br, I, nitro, CF₃, R₁CF₂Z⁻, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N and when taken together X and Y may form a ring in which XY are represented by the structure:

-OCH₂O⁻, -OCF₂O⁻ or

Z is S(O)n or O; R₁ is H, F, CHF₂, CHFCl or CF₃; R₂ is C₁-C₃ alkyl, C₁-C₃ alkoxy or R₃R₄N; R₃ is H or C₁-C₃ alkyl; R₄ is H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2; with the provisos that when R is hydrogen, R₆ is C₂-C₆ alkyl or C₅-C₆ cycloalkyl and when R₆ is hydrogen, R is C₂-C₅ alkyl or C₅-C₆ cycloalkyl; a surfactant; and an inert solid or liquid diluent therefore.

17. A composition according to Claim 16, wherein R is tert-butyl.

18. A method for protecting living plants through an extended period of active growth from insects which infest said living plants, said method characterizing: applying to the foliage of said plants or to the soil or other media in which they are growing, an insecticidally-effective amount of a compound with the formula,

wherein R and R₆ are each independently hydrogen, C₂-C₆ alkyl or C₅-C₆ cycloalkyl; X and Y are each independently H, C₁-C₃ alkyl, C₁-C₃ alkoxy, C₁-C₃ alkylthio, C₁-C₃ alkyl-sulfinyl, C₁-C₃ alkylsulfonyl, cyano, F, Cl, Br, I, nitro,
CF₃, R₁CF₂Z-, 1,1-difluoro-2,2-dichloroethoxy, R₂CO or R₃R₄N and when taken together X and Y may form a ring in which XY are represented by the structure:

\[ -\text{OCH}_2\text{O}-, -\text{OCF}_2\text{O}- \text{ or } \]

Z is S(0)n or O; R₁ is H, F, CHF₂, CHFCl or CF₃; R₂ is C₁-C₃ alkyl, C₁-C₃ alkoxy or R₃R₄N; R₃ is H or C₁-C₃ alkyl; R₄ is H, C₁-C₃ alkyl or R₅CO; R₅ is H or C₁-C₃ alkyl and n is 0, 1 or 2; with the provisos that when R is hydrogen, R₆ is C₂-C₅ alkyl or C₅-C₆ cycloalkyl and when R₆ is hydrogen, R is C₂-C₅ alkyl or C₅-C₆ cycloalkyl.

19. A method according to Claim 18, wherein said compound is applied to the foliage of plants or to the soil or other media in which they are growing at a rate of about 0.1 kg/ha to about 10.0 kg/ha.

20. A method according to Claim 18, wherein said compound is applied to the foliage of said plants or to the soil or other media in which they are growing in the form of a dilute spray containing from about 10 ppm to 10,000 ppm of the said compound.

21. A method for systemically protecting plants from insect attack, said method characterizing: applying to the soil or other media in which said plants are growing, a systemically-effective insecticidal amount of a compound with formula,
wherein \( R \) and \( R_6 \) are each independently hydrogen, \( C_2-C_6 \) alkyl or \( C_5-C_6 \) cycloalkyl; \( X \) and \( Y \) are each independently H, \( C_1-C_3 \) alkyl, \( C_1-C_3 \) alkoxy, \( C_1-C_3 \) alkylthio, \( C_1-C_3 \) alkylsulfinyl, \( C_1-C_3 \) alkylsulfonyl, cyano, F, Cl, Br, I, nitro, CF\(_3\), \( R_1CF_2Z\)-, 1,1-difluoro-2,2-dichloroethoxy, \( R_2CO \) or \( R_3R_4N \) and when taken together \( X \) and \( Y \) may form a ring in which \( XY \) are represented by the structure:

\[
\begin{align*}
-\text{OCH}_2\text{O}^- & \quad \text{or} \quad -\text{OCF}_2\text{O}^- \\
\end{align*}
\]

\( Z \) is \( \text{S(O)}_n \) or 0; \( R_1 \) is H, F, CHF\(_2\), CHFCI or CF\(_3\); \( R_2 \) is \( C_1-C_3 \) alkyl, \( C_1-C_3 \) alkoxy or \( R_3R_4N \); \( R_3 \) is H or \( C_1-C_3 \) alkyl; \( R_4 \) is H, \( C_1-C_3 \) alkyl or \( R_5CO \); \( R_5 \) is H or \( C_1-C_3 \) alkyl and \( n \) is 0, 1 or 2; with the provisos that when \( R \) is hydrogen, \( R_6 \) is \( C_2-C_5 \) alkyl or \( C_5-C_6 \) cycloalkyl and when \( R_6 \) is hydrogen, \( R \) is \( C_2-C_5 \) alkyl or \( C_5-C_6 \) cycloalkyl.

DATED this EIGHTH day of DECEMBER 1986

AMERICAN CYANAKID COMPANY

Patent Attorneys for the Applicant
SPURSON & FERGUSON