

SPECIFICATION

N-(1,3,4-Thiadiazol-2-yl)benzamides.

The present invention relates to N-(1,3,4-thiadiazol-2-yl)benzamides, having a phenyl, naphthyl or hetero-aryl group at the 5-position of the thiadiazole ring and 2,6-substitution on the benzyl ring, which are useful insecticides.

The control of insects was one of the first problems undertaken by agricultural chemical research, and continues to be pursued vigorously by the art. Insects of many orders assault crops of all types, and also cause unsanitary conditions and nuisance by contaminating foodstuffs. The damage caused by insects is incalculable, and the control of harmful insects necessarily is of the highest priority.

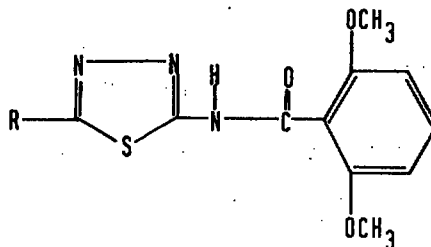
Recently, the search for new and better insecticides has been spurred by the withdrawal from use of the old residual insecticides.

The compounds of Formula I are new to organic chemistry. Some items in the prior art, however, are of interest. For example, Cebalo, U.S. Patent 3,726,892, discloses herbicidal 1,3,4-thiadiazol-2-ylureas.

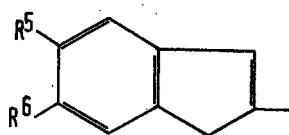
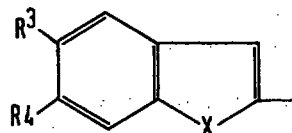
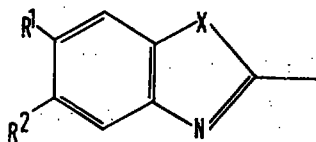
Rao, *Indian J. Chem.* 8, 509—13 (1970), teaches a synthesis method for 2-amino-1,3,4-thiadiazoles, which are intermediates for the compounds of this invention.

Wellington and Mulder, U.S. Patent 3,748,356, show herbicidal and insecticidal efficacy of N-benzoyl-N'-phenyl-ureas.

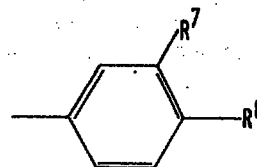
This invention belongs to the field of agricultural chemistry, and provides thiadiazolyl benzamides of the formula:



wherein R represents



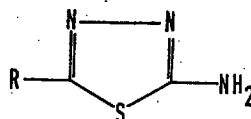
or



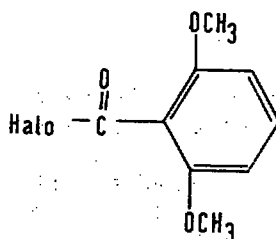
- 25 X represents oxygen or sulfur;
 one of R¹ and R² represents hydrogen and the other represents fluoro, chloro, bromo, trifluoromethyl or methoxy;
 one of R³ and R⁴ represents hydrogen and the other represents methoxy or trifluoromethyl;
 one of R⁵ and R⁶ represents hydrogen and the other represents chloro, bromo, fluoro, trifluoromethyl or hydrogen;
 one of R⁷ and R⁸ represents hydrogen and the other represents C₁—C₂ alkoxy substituted with one or more fluorine atoms.

The present invention also provides a process for preparing the compounds of Formula I, wherein R is as defined above, which comprises either

- 1) acylating a 2-amino-5-R-substituted 1,3,4-thiadiazole of the formula

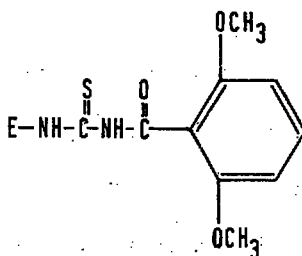


wherein R is as defined in Formula I, with a benzoyl halide of the formula



(III)

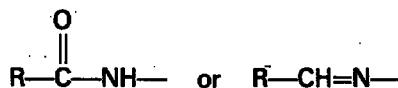
wherein Halo refers to chloro or bromo, or
2) cyclizing a compound of the formula



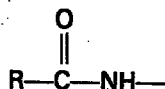
(IV)

5 wherein E represents

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wherein R is as defined in Formula I, with a dehydrating agent, when E represents

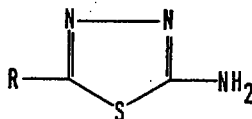


or with an oxidizing agent, when E represents $\text{R}-\text{CH}=\text{N}-$.

10 Novel insecticidal methods and insecticidal compositions making use of the novel compounds are 10 also provided.

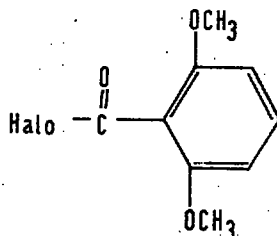
Throughout this document, all quantities are measured in the metric system, and temperatures are on the Celcius scale. All proportions and percentages are by weight. The term halogen refers to fluoro, chloro, bromo and iodo.

15 The compounds of Formula I are made by processes which are presently known or are analogous 15 to presently-known processes. All of the compounds are readily made by the acylation of 2-amino-5-R-substituted 1,3,4-thiadiazoles of the formula



(II)

wherein R is as defined in Formula I above, with benzoyl halides of the formula



(III)

20

wherein Halo refers to chloro or bromo.

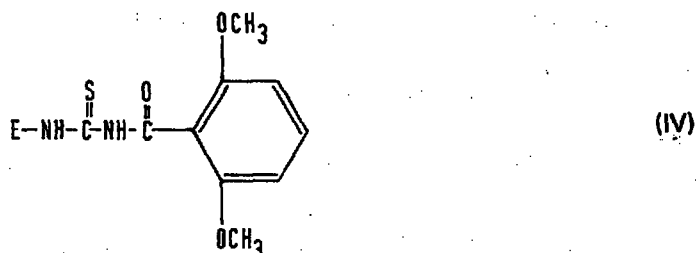
The acylation step is conveniently carried out in the presence of a base and in a reaction solvent such as tetrahydrofuran, dimethylformamide, dimethylsulfoxide or diethyl ether. The preferred base is sodium hydride, although organic bases such as pyridine, triethylamine and triethanolamine may be used, as can inorganic bases including sodium hydroxide, potassium carbonate and lithium bicarbonate. The temperature range of the reaction is conveniently from -10° to 75° , preferably from 0° to 25° .

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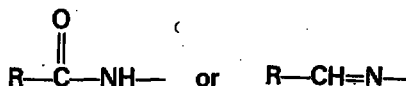
The intermediate aminothiadiazoles are prepared by reactions which are now well known. In

general, they are prepared either by oxidative cyclization of athiosemicarbazone, preferably with ferric chloride, or by dehydrative cyclization of a thiosemicarbazide with a strong acid. See, for example, Rao, *supra*, and Cebalo, *supra*.

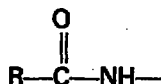
The compounds of Formula I, wherein R is as defined above, are also prepared by cyclizing a compound of the formula



wherein E represents



wherein R is as defined in Formula I, with a dehydrating agent when E represents



or with an oxidizing agent, when E represents $\text{R}-\text{CH}=\text{N}-$.

Useful dehydrating agents include phosphoric acid, formic acid, phosphorus pentachloride, phosphorus pentoxide in the presence of a strong acid, and benzoic and alkanolic acid chlorides and acid anhydrides. The preferred dehydrating agents are the strong acids, particularly methanesulfonic acid and concentrated sulfuric acid.

Dehydrative cyclizations are conveniently run at temperatures from 20° to 80°, preferably at room temperature. It is usually preferred to carry out the reactions without solvent, although solvents including the halogenated benzenes and the halogenated alkanes, including chlorobenzene, the dichlorobenzenes, chloroform and methylene dichloride, may be used if desired.

The preferred oxidizing agent is ferric chloride. Other powerful oxidizing agents can be used, for example, calcium ferricyanide. Oxidative cyclizations are preferably run in lower alkanols, for example, ethanol or propanol, at the reflux temperature of the reaction mixture. In general, however, temperatures from 50° to 100° may be used if convenient.

As organic chemists will recognize, all of the starting compounds used in preparing the compounds of Formula I are obtainable by those of ordinary skill.

The following examples show the synthesis of typical compounds, and the following preparations show the synthesis of typical starting compounds. In all of the examples, the compounds were identified by nuclear magnetic resonance analysis, elemental microanalysis, and, in some cases, by infrared analysis and mass spectroscopy.

The first group of examples illustrate the preparation of compounds of formula I by the acylation of aminothiadiazoles.

Example 1

N-[5-(4-Trifluoromethoxyphenyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide

A mixture of 1.8 ml. of pyridine and 5.2 g. of 2-amino-5-(4-trifluoromethoxyphenyl)-1,3,4-thiadiazole in 50 ml. of tetrahydrofuran was heated to the reflux temperature. A 4.4 g. portion of 2,6-dimethoxybenzoyl chloride in 20 ml. of tetrahydrofuran was added dropwise over a period of 15 minutes. The mixture was then stirred at reflux for 45 minutes more. The solvent was then removed under vacuum and the residue was recrystallized from aqueous ethanol to obtain 7.2 g. of the product named above as white needle-like crystals, m.p. 201—203°C.

Example 2

N-[5-(6-Methoxy-2-benzo[b]furyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide

To 100 ml. of tetrahydrofuran containing 0.7 g. of 2-amino-5-(6-methoxy-2-benzo[b]furyl)furyl)-1,3,4-thiadiazole was added 0.3 g of sodium hydride. After the bubbling had ceased, 0.62 g. of 2,6-dimethoxybenzoyl chloride was added. The reaction mixture was stirred for 1 hour at room temperature, and the solvent was removed by evaporation under vacuum. Water was added to the residue, and it was made acid with 1N hydrochloric acid. The solids were collected by filtration, dried and recrystallized from benzene-hexane to obtain 0.12 g. of the product named above, m.p. 215—217°C.

Synthesis of the following exemplary compounds followed, in general, the process of Example 1 and 2. In each example below, the substituents of the aminothiadiazole and the benzoyl halide are obvious from the name of the product. The exemplary compound will first be named, and then the amounts of the reactants and the amounts and melting points of the products will be tabulated.

5 **Example 3**

N-[5-(2-Indenyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide

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Example 4

N-[5-(5-Methoxy-2-benzo[b]furyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide

Example 5

10 N[5-(5-Trifluoromethyl-2-benzo[b]furyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide

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Example 6

N-[5-(6-Trifluoromethyl-2-benzo[b]furyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide.

Example 7

N-[5-(4-Pentafluoroethoxyphenyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide.

15 **Example 8**

N-[5-(5-Fluoro-2-benzo[b]furyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide.

15

Example

No.	Aminothiadiazole	Benzoyl Chloride	Product	M.P., °C.
3	1.0	1.0	0.2	230—232
4	2.0	1.8	1.3	255—257
5	2.8	2.2	2.5	242—245
6	2.0	1.6	1.0	206—208
7	3.1	2.2	1.7	227—229
8	2.4	2.2	1.7	244—245

25 The next group of preparations and examples illustrate typical cyclizations with dehydrating agents.

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Preparation 1

1-(4-Pentafluoroethoxybenzoyl)-4-(2,6-dimethoxybenzoyl)-thiosemicarbazide

A 0.54 g. portion of ammonium thiocyanate was added to 10 ml. of tetrahydrofuran, the mixture was heated to the reflux temperature, and to it was added 1.5 g. of 2,6-dimethoxybenzoyl chloride dissolved in 10 ml. of additional tetrahydrofuran. The mixture was stirred at the reflux temperature for 20 minutes, cooled to the ambient temperature, and 1.5 g. of 4-pentafluoroethoxybenzoyl-hydrazine, dissolved in 20 ml. of tetrahydrofuran, was added dropwise. The reaction mixture was stirred at ambient temperature for 1.5 hours. Then the mixture was evaporated to dryness under vacuum, and the residue was washed with diethyl ether. The ether was then concentrated under vacuum and the product was recrystallized to produce 1.1 g. of the compound named above, m.p. 184—186°C.

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Example 9

N-[5-(4-Pentafluoroethoxyphenyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide

A 1 g. portion of the intermediate prepared in Preparation 1 was slowly added to 5 g. of methanesulfonic acid, and the mixture was stirred at ambient temperature for 5 hours. The mixture was then poured slowly onto 100 g. of ice and stirred thoroughly. The pH of the aqueous mixture was then brought to 8.5 by the addition of concentrated ammonium hydroxide, and the solids were collected by filtration and recrystallized from aqueous ethanol to obtain 0.6 g. of a crude product. The product was purified by chromatography over silica gel with a solvent consisting of 70 percent toluene and 30 percent ethyl acetate. The purified yield was 200 mg. of the product named in the heading above, identical to the product of Example 7.

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Example 10

N-[5-(4-Trifluoromethoxyphenyl)-1,3,4-thiadiazol-yl]-2,6-dimethoxybenzamide

The process of Example 9 is used, starting with 1-(4-trifluoromethoxybenzoyl)-4-(2,6-dimethoxybenzoyl)-thiosemicarbazide to prepare the compound named above, identical to the product of Example 1, by reaction with methanesulfonic acid.

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Example 11

N-[5-(6-Methoxy-2-benzo[b]furyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide

A portion of 1-(6-methoxy-2-benzo[b]furylcarbonyl)-4-(2,6-dimethoxybenzoyl)thiosemicarbazide is reacted with methanesulfonic acid to obtain the product named above, identical to the product of Example 2, according to the process of Example 9.

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Example 12**N-[5-(2-Indenyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide**

The process of Example 9 is used to prepare the product named above, identical to the product of Example 3 by reaction of 1-(2-indenocarbonyl)-4-(2,6-dimethoxybenzoyl)-thiosemicarbazide with methanesulfonic acid.

Example 13**N-[5-(5-Methoxy-2-benzo[b]furyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide**

According to the process of Example 9, methane-sulfonic acid is reacted with 1-(5-methoxy-2-benzo[b]furyl-carbonyl)-4-(2,6-dimethoxybenzoyl)thiosemicarbazide to obtain the product named above, identical to the product of Example 4.

Example 14**N-[5-(5-Trifluoromethyl-2-benzo[b]furyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide**

A portion of 1-(5-trifluoromethyl-2-benzo[b]furylcarbonyl)-4-(2,6-dimethoxybenzoyl)thiosemicarbazide is reacted with methanesulfonic acid as described in Example 9 to obtain the product named above, identical to the product of Example 5.

Example 15**N-[5-(6-Trifluoromethyl-2-benzo[b]furyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide**

The general process of Example 9 is followed by reacting 1-(6-trifluoromethyl-2-benzo[b]furylcarbonyl)-4-(2,6-dimethoxybenzoyl)thiosemicarbazide with methane-sulfonic acid to obtain the product named above, identical to the product of Example 6.

Example 16**N-[5-(5-Fluoro-2-benzo[b]furyl)-1,3,4-thiadiazol-2-yl]-2,6-dimethoxybenzamide**

As described in Example 9, 1-(5-fluoro-2-benzo[b]furylcarbonyl)-4-(2,6-dimethoxybenzoyl)thiosemicarbazide is reacted with methanesulfonic acid to obtain the product named in the heading above, identical to the product of Example 8.

The compounds of Formula I have been thoroughly tested against live insects to determine the range of their insecticidal efficacy. The following tests are typical of the experiments performed and the results obtained.

In many instances, repeated tests at an application rate have been performed, and the results of such tests have been averaged. Blank spaces in the data tables below indicate that no test at the named application rate has been done. Compounds are identified by their example numbers.

Test 1**Mexican bean beetle and southern armyworm test**

Each compound to be tested was formulated by dissolving 10 mg. of the compound in 1 ml. of solvent comprising 1:1 anhydrous ethanol: acetone containing 23 g. of Toximul R and 13g. Toximul S per liter. (Toximuls are trademarks for sulfonate/nonionic blended surfactants produced by Stepan Chemical CO., Northfield, Illinois, U.S.A.). Each sample was then dispersed in 9 ml. of water to provide a 1000 ppm. concentration of the test compound. This dispersion was diluted with water to produce lower concentrations, when desired. The dispersion was sprayed evenly over ten-day-old bean plants and the plants were set aside until dry.

Leaves were then removed from the plants, and the cut ends of the leaves were wrapped in water-soaked cotton. Two leaves were placed in each 100-mm. plastic petri dish, and 5 second- or third-instar Mexican bean beetle larvae (*Epilachna varivestis*) and 5 second- or third-instar southern armyworm larvae (*Spodoptera eridania*) were placed in each dish. Three replicate dishes were used for each test compound. The dishes were held at about 25° and 51 percent relative humidity for 4 days, and the first evaluation of the insecticidal efficacy was made. Some of the dishes were held in the controlled room for three days more, and another evaluation was made.

Insecticidal efficacy was rated on the following scale, compared to solvent controls and nontreated controls.

0=no control
1=1—7 larvae dead
2=8—14 larvae dead
3=15 larvae dead

The following table reports the results of testing typical compounds.

Table 1
Mexican bean
beetle

Southern
armyworm

Compound of Example No.	Appln. Rate ppm.	Mexican bean beetle		Southern armyworm		
		4 day	7 day	4 day	7 day	
5	2	1000	2	2	2	5
		100	1	1	2	
	3	1000	0	3	3	
		100	0	2	3	
10	4	1000	0	0	0	10
		100	0	0	0	
	5	1000	0	3	3	
		100	0	3	3	
	6	1000	0	3	3	
		100	0	2	3	
15	7	1000	2	3	3	15
		100	2	3	3	
	8	1000	2	3	3	
		100	1	3	3	

The compound of Example 1 was tested in the same test method but at different application rates, and the number of insect larva which were killed was evaluated as a percentage kill, rather than on the 0—3 scale. In a 4-day test against southern armyworm larvae, the compound produced 100 percent kill at 5 ppm., and produced 100 percent kill at 2.5 ppm. in a 7-day test. In a test against the Mexican bean beetle, the compound produced 100 percent kill in 4 days at the application rate of 5 ppm., and produced 80 percent kill in 7 days at 2.5 ppm.

The above illustrative data show the potent insecticidal effect of the compounds of Formula I. Entomologists will understand that the compounds are broadly useful for the control of insects of the various orders which adversely affect mankind and its economic enterprises.

For example, the compounds control Coleoptera such as *Anthonomus grandis*, *Crambus caliginosellus*, *Oulema melanopus*, *Leptinotarsa decemlineata*, *Hyper postica*, *Anthrenus scrophulariae*, *Tribolium confusum*, *Lyctidae* species, *Agriotes* species, *Sitophilus oryzae*, *Nodonta puncticollis* and *Conotrachelus neruphar*; Diptera such as *Musca domestica*, *Stomoxys calcitrans*, *Haematobia irritans*, *Phormia regina*, *Hylemya brassicae* and *Psila rosae*; Lepidoptera, such as *Laspeyresia pomonella*, *Euxoa* species, *Plodia interpunctella*, *Tartridae* species, *Heliothis zea*, *Ostrinia nubilalis*, *Hellula rogatalis*, *Trichoplusia ni*, *Thyridopteryx ephemeraeformis*, *Malacosoma americanum* and *Spodoptera frugiperda*; and Orthoptera, such as *Blattella germanica* and *Periplaneta americana*.

The compounds are useful for reducing populations of insects, and are used in a method of reducing an insect population which comprises applying an insecticidally-effective amount of one of the compounds to a substance to be ingested by the insects.

Insects may be caused to ingest a compound by applying the compound to any substance which they ingest. For example, plant-infesting insects are readily controlled by applying a compound to plant parts which the insects eat, particularly the foliage. Insects which infest and consume textiles, paper, wood products and the like are readily controlled by applying a compound to such products. The compounds can similarly be effectively used to protect stored grain or seeds.

It is notable that the compounds interfere with the formation of successive stages of insects which ingest them. For example, when adult insects ingest the compounds, the adults are grossly unaffected, but lay sterile eggs. When an insect larva consumes a compound, it dies without metamorphosing into the next larval stage. Last-stage larvae which consume a compound pupate, but die in the pupa form.

Entomologists will understand that it is not inferred that use of a compound of Formula I will necessarily result in the extinction of an insect population. In some instances, of course, the whole population will be killed. In other instances, part of the insects will be killed and others will survive treatment with the compound. The portion of the population which will be killed depends upon the species of insect, the particular compound in use, the application rate, the vigor of the insects, the weather and other factors understood by entomologists. Thus, the term "reducing a population of insects" refers to a decrease in the numbers of living insects, which in some but not all instances will amount to the disappearance of the population of treated insects.

The extent of population reduction accomplished by a compound depends, of course, upon the application rate of the compound. At least an insecticidally-effective amount must be used in all cases. The term "insecticidally-effective amount" is used to describe an amount which is sufficient to cause a measurable reduction in the treated insect population. Insecticidally-effective amounts are found, in general, in the range from 1 to 1000 ppm.

It will be understood that application rates of insecticides are usually measured in terms of the concentration of the insecticide in the dispersion in which it is applied. The application rate is measured in this way because it is most convenient to apply a sufficient amount of the dispersion to cover the

foliage, or other substance to be treated, with a thin film of the dispersion. The amount of dispersion applied is thus dependent upon the surface area of the ingestable substance to be treated, and the amount of the compound depends on its concentration in the dispersion.

The dispersions in which the compounds are applied are prepared from typical insecticidal compositions which are, however, novel because of the presence of the novel compounds of this invention. Most widely useful are aqueous dispersions prepared by mixing a small amount of a concentrated insecticidal composition with an appropriate quantity of water to give the desired concentration of the compound. Such concentrated water-dispersible compositions, containing in general from 5 to 90 percent of the compound, are usually in the form of emulsifiable concentrates, wettable powders or suspensions.

Wettable powders comprise an intimate mixture of the active compound in an inert carrier which is a mixture of a fine inert powder and surfactants. The concentration of the active compound is usually from about 10 percent to about 90 percent by weight. The inert powder is usually chosen from among the attapulgite clays, the montmorillonite clays, the diatomaceous earths, or the purified silicates. Effective surfactants, comprising from 0.5 percent to 10 percent of the wettable powder, are found among the sulfonated lignins, the condensed naphthalenesulfonates, the naphthalenesulfonates, the alkylbenzenesulfonates, the alkyl sulfates, and nonionic surfactants such as ethylene oxide adducts of alkyl phenol.

Typical emulsifiable concentrates of the compounds comprise a convenient concentration of the compound, such as from 50 to 500 g. per liter of liquid, equivalent to from 5 percent to 50 percent, dissolved in an inert carrier which is a mixture of water-immiscible organic solvent and emulsifiers. Useful organic solvents include the aromatics, especially the xylenes, and the petroleum fractions, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy aromatic naphtha. Other organic solvents may also be used, such as the terpenic solvents including resin derivatives, and complex alcohols such as 2-ethoxyethanol. Suitable emulsifiers for emulsifiable concentrates are chosen from the same types and concentrations of surfactants used for wettable powders.

Suspensions of the compounds comprise a concentration of the compound similar to the concentration in an emulsifiable concentrate, in the form of a finely divided powder, suspended in a suitable non-solvent liquid. The most suitable non-solvent liquid is a mixture of water and surfactants. The same types of surfactants used for wettable powders are used in making suspensions. In many instances, a small quantity of an inert diluent is used to improve the suspending properties. Such inert diluents include swellable clays such as attapulgite and montmorillonite, starches and especially purified silicates.

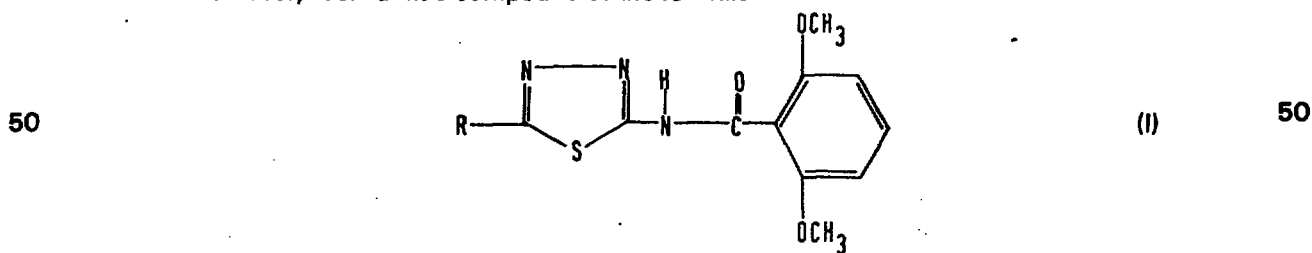
It is equally practical, when desirable for any reason, to apply the compound in the form of a solution in an appropriate organic solvent, usually a bland petroleum oil such as the spray oils which are widely used in agricultural chemistry.

Further, the compounds may be applied as compositions in the forms of dusts and aerosol preparations. Dusts comprise a compound in a finely powdered form, dispersed in a powdered inert carrier. The carrier is usually a powdered clay, such as pyrophyllite, bentonite, a volcanic deposit or montmorillonite. Dusts usually contain concentrations of the compound in the range of from 0.1 percent to 10 percent.

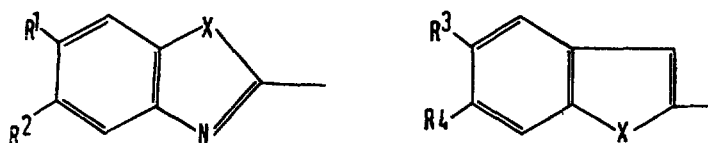
Aerosol compositions comprise a compound of Formula I dissolved or dispersed in an inert carrier which is a pressure-generating propellant mixture and packaged in a container from which the mixture is dispensed through an atomizing valve. Propellant mixtures comprise either low-boiling halocarbons, which may be mixed with organic solvents, or aqueous suspensions pressurized with inert gases or gaseous hydrocarbons.

Claims

1. A thiadiazolyl benzamide compound of the formula



wherein R represents





17 18

foliage, or other substance to be treated, with a thin film of the dispersion. The amount of dispersion applied is thus dependent upon the surface area of the ingestable substance to be treated, and the amount of the compound depends on its concentration in the dispersion.

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Wettable powders comprise an intimate mixture of the active compound in an inert carrier which is a mixture of a fine inert powder and surfactants. The concentration of the active compound is usually from about 10 percent to about 90 percent by weight. The inert powder is usually chosen from among the attapulgite clays, the montmorillonite clays, the diatomaceous earths, or the purified silicates. Effective surfactants, comprising from 0.5 percent to 10 percent of the wettable powder, are found among the sulfonated lignins, the condensed naphthalenesulfonates, the naphthalenesulfonates, the alkylbenzenesulfonates, the alkyl sulfates, and nonionic surfactants such as ethylene oxide adducts of alkyl phenol.

Typical emulsifiable concentrates of the compounds comprise a convenient concentration of the compound, such as from 50 to 500 g. per liter of liquid, equivalent to from 5 percent to 50 percent, dissolved in an inert carrier which is a mixture of water-immiscible organic solvent and emulsifiers. Useful organic solvents include the aromatics, especially the xylenes, and the petroleum fractions, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy aromatic naphtha. Other organic solvents may also be used, such as the terpenic solvents including resin derivatives, and complex alcohols such as 2-ethoxyethanol. Suitable emulsifiers for emulsifiable concentrates are chosen from the same types and concentrations of surfactants used for wettable powders.

Suspensions of the compounds comprise a concentration of the compound similar to the concentration in an emulsifiable concentrate, in the form of a finely divided powder, suspended in a suitable non-solvent liquid. The most suitable non-solvent liquid is a mixture of water and surfactants. The same types of surfactants used for wettable powders are used in making suspensions. In many instances, a small quantity of an inert diluent is used to improve the suspending properties. Such inert diluents include swellable clays such as attapulgite and montmorillonite, starches and especially purified silicates.

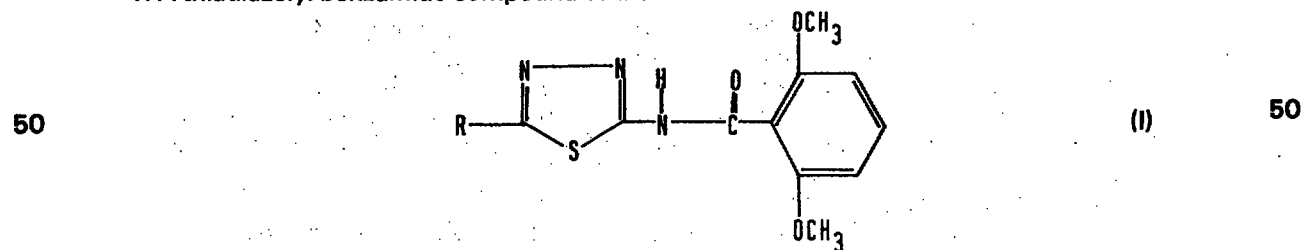
It is equally practical, when desirable for any reason, to apply the compound in the form of a solution in an appropriate organic solvent, usually a bland petroleum oil such as the spray oils which are widely used in agricultural chemistry.

Further, the compounds may be applied as compositions in the forms of dusts and aerosol preparations. Dusts comprise a compound in a finely powdered form, dispersed in a powdered inert carrier. The carrier is usually a powdered clay, such as pyrophyllite, bentonite, a volcanic deposit or montmorillonite. Dusts usually contain concentrations of the compound in the range of from 0.1 percent to 10 percent.

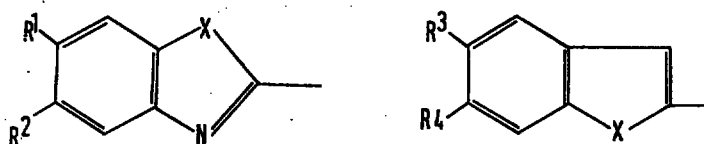
Aerosol compositions comprise a compound of Formula I dissolved or dispersed in an inert carrier which is a pressure-generating propellant mixture and packaged in a container from which the mixture is dispensed through an atomizing valve. Propellant mixtures comprise either low-boiling halocarbons, which may be mixed with organic solvents, or aqueous suspensions pressurized with inert gases or gaseous hydrocarbons.

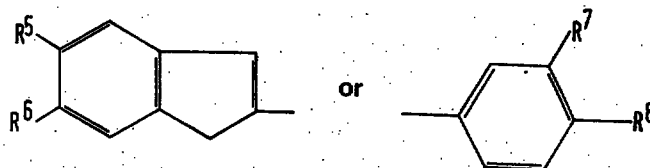
Claims

1. A thiadiazolyl benzamide compound of the formula



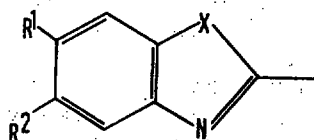
wherein R represents



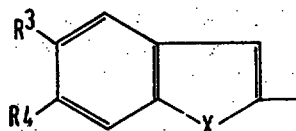


X represents oxygen or sulfur;
one of R¹ and R² represents hydrogen and the other represents fluoro, chloro, bromo, trifluoromethyl or methoxy;
one of R³ and R⁴ represents hydrogen and the other represents methoxy or trifluoromethyl;
one of R⁵ and R⁶ represents hydrogen and the other represents chloro, bromo, fluoro, trifluoromethyl or hydrogen;
one of R⁷ and R⁸ represents hydrogen and the other represents C₁—C₂ alkoxy substituted with one or more fluorine atoms.

2. A compound of Formula I of claim 1 wherein R represents

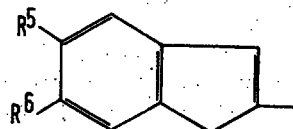


3. A compound of Formula I of claim 1, wherein R represents

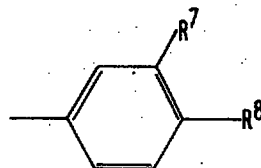


4. A compound of Formula I of claim 3 wherein R represents substituted benzofuryl.
5. A compound of Formula I of claim 4 wherein R represents 6-methoxy-2-benzo[b]furyl.
6. A compound of Formula I of claim 4 wherein R represents 5-methoxy-2-benzo[b]furyl.
7. A compound of Formula I of claim 4 wherein R represents 5-trifluoromethyl-2-benzo[b]furyl.
8. A compound of Formula I of claim 4 wherein R represents 6-trifluoromethyl-2-benzo[b]furyl.
9. A compound of Formula I of claim 4 wherein R represents 5-fluoro-2-benzo[b]furyl.

10. A compound of Formula I of claim 1 wherein R represents



11. A compound of Formula I of claim 10 wherein R represents 2-indenyl.
12. A compound of Formula I of claim 1 wherein R represents



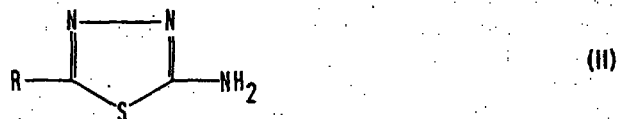
13. A compound of Formula I of claim 12 wherein R⁷ represents hydrogen.
14. A compound of Formula I of claim 13 wherein R⁸ represents C₁—C₂ perfluoroalkoxy.
15. A compound of Formula I of claim 14 wherein R represents 4-trifluoromethoxyphenyl.
16. A compound of Formula I of claim 14 wherein R represents 4-pentafluoroethoxyphenyl.
17. An insecticidal composition which comprises an inert carrier and a thiadiazolyl benzamide compound of Formula I as defined in any of claim 1—16.
18. An insecticidal composition of claim 17 which is a wettable powder.
19. An insecticidal composition of claim 17 which is an emulsifiable concentrate.
20. An insecticidal composition of claim 17 which is a suspension.
21. A method of reducing an insect population which comprises applying an insecticidally-effective amount of a compound of Formula I as defined in any of claims 1—16 to a substance to be ingested by the insects.
22. A method of reducing an insect population which comprises applying an insecticidally-effective amount of a compound of Formula I in the form of an insecticidal composition as defined in any of claims 17—20 to a substance to be ingested by the insects.



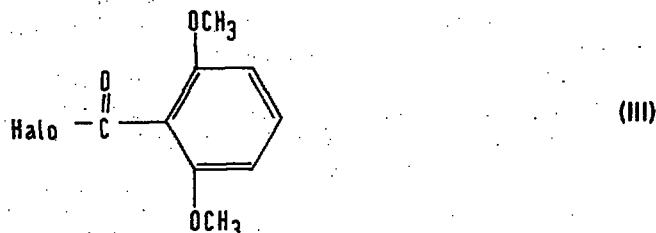
19/18

23. A process for preparing a compound of Formula I, as defined in claim 1, which process comprises either:

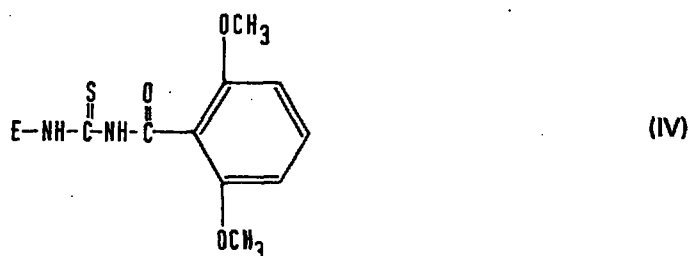
1) acylating a 2-amino-5-R-substituted 1,3,4-thiadiazole of the formula



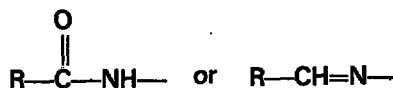
5 wherein R is as defined in Formula I, with a benzoyl halide of the formula



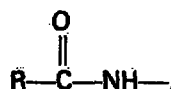
wherein Halo refers to chloro or bromo, or
2) cyclizing a compound of the formula



10 wherein E represents



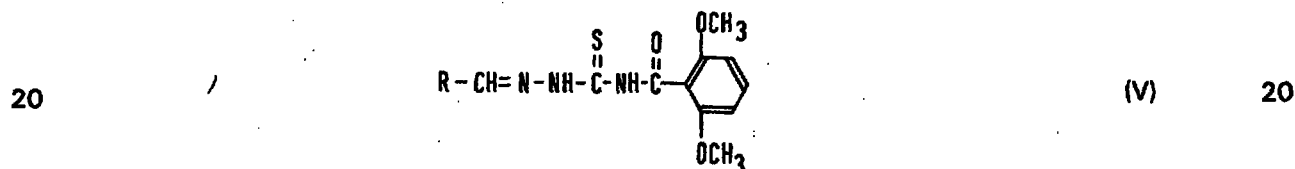
wherein R is as defined in Formula I, with a dehydrating agent, when E represents



or with an oxidizing agent, when E represents $\text{R} - \text{CH} = \text{N} -$.

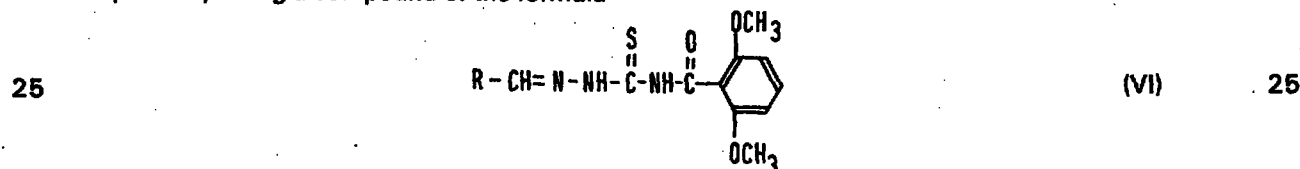
15 24. A process of claim 23 for preparing a compound of Formula I, as defined in claim 1, which process comprises acylating a compound of Formula II as defined in claim 23, with a benzoyl halide of Formula III, as defined in claim 23. 15

25. A process of claim 23 for preparing a compound of Formula I, as defined in claim 1, which comprises cyclizing a compound of the formula



wherein R is as defined in claim 1,
with an oxidizing agent.

26. A process for preparing a compound of Formula I, as defined in claim 1, which process comprises cyclizing a compound of the formula



wherein R is as defined in claim 1,
with a dehydrating agent.

27. A process for preparing a compound of Formula I, wherein R is as defined in any of claims 2—16, which process comprises acylating a compound of Formula II, wherein R is as defined in any of claims 2—16, with a benzoyl halide of Formula III, as defined in claim 23.
28. A process for preparing a compound of Formula I, wherein R is as defined in any of claims 2—16, which process comprises cyclizing a compound of Formula V, wherein R is as defined in any of claims 2—16, with an oxidizing agent. 5
29. A process for preparing a compound of Formula I, wherein R is as defined in any of claims 2—16, which process comprises cyclizing a compound of Formula VI, wherein R is as defined in any of claims 2—16, with a dehydrating agent.
- 10 30. A process of claim 29 wherein the dehydrating agent is methanesulfonic acid. 10
31. A compound of Formula I as claimed in claim 1, substantially as hereinbefore described with particular reference to any one of the examples.
32. An insecticidal composition as claimed in claim 17, substantially as hereinbefore described.
33. An insecticidal method as claimed in claim 21, substantially as hereinbefore described.
- 15 34. A process as claimed in claim 23, substantially as hereinabove described with particular reference to any one of the examples. 15

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1982. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

