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PYRROLE THIOCARBOXAMIDE INSECTICIDAL AND

ACARICIDAL AGENTS

In spite of the commercial insecticides and acaricides available today, damage to crops, both growing and harvested, caused by insects and acarina still occurs. Accordingly, there is ongoing research to create new and more effective insecticides and acaricides.

It is therefore an object of the present invention to provide pyrrole thiocarboxamide compounds which are highly effective for controlling insects and acarina.

It is also an object of the present invention to provide a method for protecting growing plants from attack by insects and acarina by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally or acaricidally effective amount of a pyrrole thiocarboxamide compound.

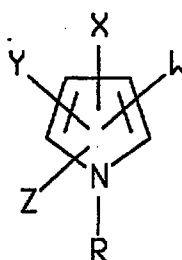
These and other objects of the present invention will become more apparent from the detailed description thereof set forth below.

The present invention describes pyrrole thiocarboxamide compounds which are highly effective insecticidal and acaricidal agents useful for the control of insect and acarid pests and for protecting agronomic crops from attack by said pests.

This invention also relates to insecticidal and acaricidal compositions containing those compounds

and methods for using those compounds and compositions for the control of insects and acarina and for the protection of growing or harvested plants from attack by insects and acarina.

5 The insecticidal and acaricidal pyrrole thiocarboxamide compounds of the present invention have the following structural formula I:



15 wherein

$$\begin{array}{c} \text{S} \\ || \\ \text{W is } \text{CNR}_1\text{R}_2; \end{array}$$

R_1 and R_2 are each independently hydrogen,

$\text{C}_1\text{-C}_4$ alkyl optionally substituted with one or more halogen atoms, or

20 phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

25 $\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or

$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;

X is Cl, Br, CN, NO_2 , O,

30 $\text{C}_1\text{-C}_4$ alkyl substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

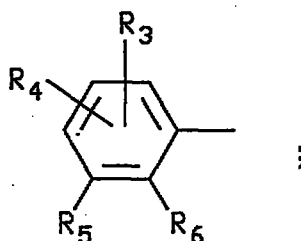
35 CN groups,

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C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

Q is



R₃ and R₄ are each independently hydrogen, halogen,
NO₂, CN or C₁-C₄ alkyl optionally substituted with
one or more halogen atoms;

R₅ and R₆ are taken together with the atoms to which
they are attached to form a 5- or 6-membered
heterocyclic ring containing 1 or 2 oxygen atoms
and optionally substituted with one or more
halogen atoms or C₁-C₄ alkyl groups optionally
substituted with one or more halogen atoms;

Y is hydrogen, Cl, Br, CN, NO₂, S(O)_nT, Q,
C₁-C₄ alkyl substituted with one or more halogen
atoms, or

phenyl optionally substituted with one or more
halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

Z is hydrogen, Cl, Br, S(O)_nT or C₁-C₄ alkyl substi-
tuted with one or more halogen atoms;

T is C₁-C₄ alkyl substituted with one or more halogen
atoms;



n is an integer of 0, 1 or 2;

R is A, OA or CN;

A is hydrogen, $\overset{\text{O}}{\parallel}\text{CR}_7$, $\overset{\text{O}}{\parallel}\text{CHR}_8\text{NHCR}_9$, CH_2SO_1 ,

- 5 $\text{C}_1\text{-C}_6$ alkyl optionally substituted with one to three halogen atoms,
one tri($\text{C}_1\text{-C}_4$ alkyl)silyl,
one hydroxy,
one cyano,
10 one or two $\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one to three halogen atoms,
one $\text{C}_1\text{-C}_4$ alkylthio,
one phenyl optionally substituted with one to three halogen atoms, one to three $\text{C}_1\text{-C}_4$ alkyl groups or one to three $\text{C}_1\text{-C}_4$ alkoxy groups,
15 one phenoxy group optionally substituted with one to three halogen atoms, one to three $\text{C}_1\text{-C}_4$ alkyl groups or one to three $\text{C}_1\text{-C}_4$ alkoxy groups,
20 one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three $\text{C}_1\text{-C}_4$ alkyl groups or one to three $\text{C}_1\text{-C}_4$ alkoxy groups,
25 one $\text{C}_1\text{-C}_6$ alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
30 one $\text{C}_2\text{-C}_6$ alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
one phenylcarbonyloxy group optionally sub-





stituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups, one C_1-C_6 alkoxycarbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or

one benzylcarbonyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

C_3-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group, or C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group;

R_7 is C_1-C_6 alkyl or C_3-C_6 cycloalkyl each optionally substituted with one to three halogen atoms, one hydroxy, one cyano, one or two C_1-C_4 alkoxy groups optionally substituted with one to three halogen atoms, one C_1-C_4 alkylthio, one phenyl group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups, one phenoxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups, one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl



groups or one to three C_1-C_4 alkoxy groups,

one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,

5 one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,

one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

10 one C_1-C_6 alkoxy carbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or

15 one benzyloxycarbonyl group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

20 C_2-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group,

C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group,

25 phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, phenoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,

30 phenoxy optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, C_1-C_4 alkylthio groups,

35



tri(C₁-C₄alkyl)silyl groups, C₁-C₄ alkyl-sulfinyl groups, C₁-C₄ alkylsulfonyl groups, CN groups, NO₂ groups or CF₃ groups,

1- or 2-naphthyl,

2-, 3-, or 4-pyridyl optionally substituted with one to three halogen atoms,

C₁-C₆ alkoxy optionally substituted with one to three halogen atoms, or

C₂-C₆ alkenyloxy optionally substituted with one to three halogen atoms;

R₈ is hydrogen or C₁-C₄ alkyl;

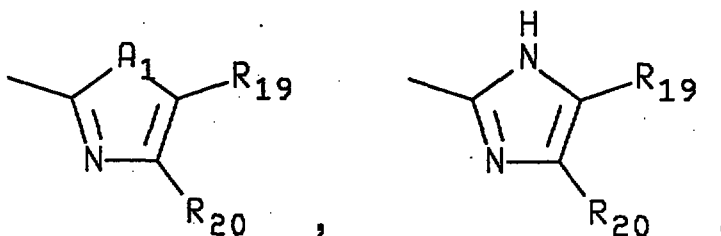
R₉ is C₁-C₆ alkyl optionally substituted with one to three halogen atoms,

phenyl optionally substituted with one to three halogen atoms, CN groups, NO₂ groups, C₁-C₄ alkyl groups, C₁-C₄ alkoxy groups or CF₃ groups,

2- or 3-thienyl, or

2- or 3-furyl;

Q₁ is $\begin{array}{c} \text{A}_1 \\ \parallel \\ \text{C}-\text{R}_{10} \end{array}$, $\begin{array}{c} \text{A}_1 \\ \parallel \\ \text{C}-\text{OR}_{11} \end{array}$, $\begin{array}{c} \text{A}_1 \\ \parallel \\ \text{C}-\text{NR}_{12}\text{R}_{13} \end{array}$, $\begin{array}{c} \text{A}_1 \\ \parallel \\ \text{P}(\text{OR}_{14})_2 \end{array}$, $\begin{array}{c} \text{NR}_{15} \\ \parallel \\ \text{C}-\text{NR}_{16}\text{R}_{17} \end{array}$,
 $\begin{array}{c} \text{NR}_{15} \\ \parallel \\ \text{C}-\text{A}_1\text{R}_{18} \end{array}$,



CN,

C₁-C₆ alkyl optionally substituted with one or more halogen atoms, CN groups or phenyl groups, or

phenyl optionally substituted with one or more



halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO_2 groups, CF_3 groups or $NR_{21}R_{22}$ groups;

A_1 is O or S;

5 R_{10} is C_1-C_6 alkyl or phenyl;

R_{11} is C_1-C_6 alkyl;

R_{12} and R_{13} are each independently hydrogen, C_1-C_6 alkyl or may be taken together with the atom to which they are attached to form a 5- to 7-membered ring;

10 R_{14} is C_1-C_4 alkyl;

R_{15} is hydrogen, C_1-C_4 alkyl or may be taken together with either R_{16} or R_{18} and the atoms to which they are attached to form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

15

R_{16} and R_{17} are each independently hydrogen or C_1-C_4 alkyl;

R_{18} is C_1-C_4 alkyl or when taken together with R_{15} and the atoms to which they are attached may form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

20

R_{19} and R_{20} are each independently hydrogen or C_1-C_4 alkyl or when taken together may form a ring wherein $R_{19}R_{20}$ is represented by $-CH=CH-CH=CH-$; and

25

R_{21} and R_{22} are each independently hydrogen or C_1-C_4 alkyl;

with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.

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Preferred formula I insecticidal and acaricidal pyrrole thiocarboxamide compounds of the invention are those wherein

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W is CNR_1R_2 ;



R_1 and R_2 are each independently hydrogen or C_1-C_4 alkyl;

X is Q or phenyl optionally substituted with one or more halogen atoms,

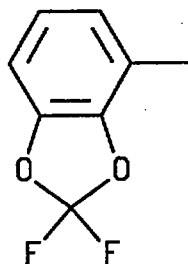
NO₂ groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Q is



Y is hydrogen, Cl, Br, CN, NO₂ or CF₃;

Z is hydrogen, Cl, Br or CF₃;

R is A or CN;

A is hydrogen, $\overset{\text{O}}{\parallel}\text{CR}_7$ or

C_1-C_6 alkyl optionally substituted with one to three halogen atoms,

one C_1-C_4 alkoxy group,

one cyano,

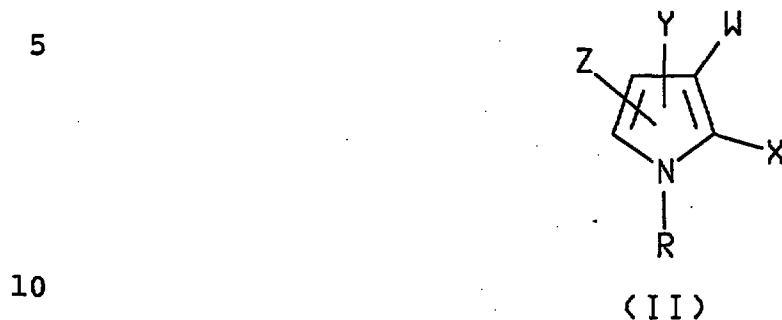
one C_1-C_6 alkylcarbonyloxy group,

one benzylcarbonyloxy group, or

one phenylcarbonyloxy group optionally substituted with one to three halogen atoms or one C_1-C_4 alkyl group; and

R_7 is phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO₂ groups or CF₃ groups.

More preferred compounds of the present invention are illustrated by formula II and formula III:



wherein

- 15 W is CNR_1R_2 ;
 R_1 and R_2 are each independently hydrogen or $\text{C}_1\text{-C}_4$ alkyl;
X is Q or phenyl optionally substituted with one or more halogen atoms,
20 NO_2 groups,
CN groups,
 $\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or
 $\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted
25 with one or more halogen atoms;

Q is



- 35 Y is hydrogen, Cl, Br or CF_3 ;
Z is Cl, Br or CF_3 ; and

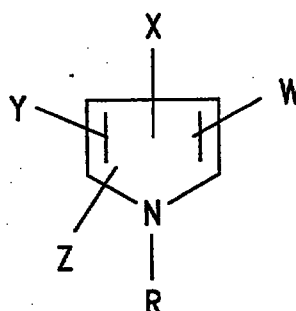




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R is hydrogen or C_1 - C_6 alkyl substituted with one C_1 - C_4 alkoxy group.

The present invention also relates to novel pyrrole thiocarboxamide compounds having the structural formula



wherein W, X, Y, Z and R are as described hereinabove for formula I with the proviso that when W is on the 3-position of the pyrrole ring and X is on the 4-position of the pyrrole ring and Y, Z and R are each hydrogen, then X is other than 2- or 3-chlorophenyl; and with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H; and with the further proviso that when R_1 and R_2 are both H, then X and Y are other than phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms.

Exemplary of halogen hereinabove are fluorine, chlorine, bromine and iodine.

Advantageously, the present invention provides a method for controlling insects and acarina by contacting said insects and acarina, their breeding



grounds, food supply or habitat with an insecticidally or acaricidally effective amount of a formula I, pyrrole thiocarboxamide compound, provided that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.

The present invention also provides a method for protecting growing plants from attack by insects and acarina by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally or acaricidally effective amount of a formula I, pyrrole thiocarboxamide compound, provided that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.

In practice generally about 10 ppm to 10,000 ppm and preferably 100 ppm to about 5,000 ppm of a formula I pyrrole thiocarboxamide compound, dispersed in water, or another liquid carrier, is effective when applied to the plants, the crops or the soil in which said crops are growing to protect said crops from attack by insects and acarina.

The formula I compounds of this invention are also effective for controlling insects and acarina, when applied to the foliage of plants and/or to the soil or water in which said plants are growing in sufficient amount to provide a rate of from about 0.100 kg/ha to 4.0 kg/ha of active ingredient.

While the compounds of this invention are effective for controlling insects and acarina when employed alone, they may also be used in combination with insecticidally and acaricidally effective amounts of one or more other biological chemicals. For example, the formula I compounds of this invention may be used effectively in conjunction or combination with phosphates, carbamates, cyclodienes, endotoxin of bacillus thuringiensis (Bt), phenol tin compounds,

pyrethroids, formamidines, chlorinated hydrocarbons, benzoylphenyl ureas and the like.

5 The compounds of the invention may be formulated as emulsifiable concentrates, flowable concentrates, or wettable powders which are diluted with water or other suitable polar solvent, generally in situ, and then applied as a dilute spray. Said compounds may also be formulated in dry compacted granules, granular formulations, dusts, dust concentrates, 10 suspension concentrates, microemulsions and the like all of which lend themselves to seed, soil, water and/or foliage applications to provide the requisite plant protection. Such formulations include the compounds of the invention admixed with inert, solid or liquid diluents.

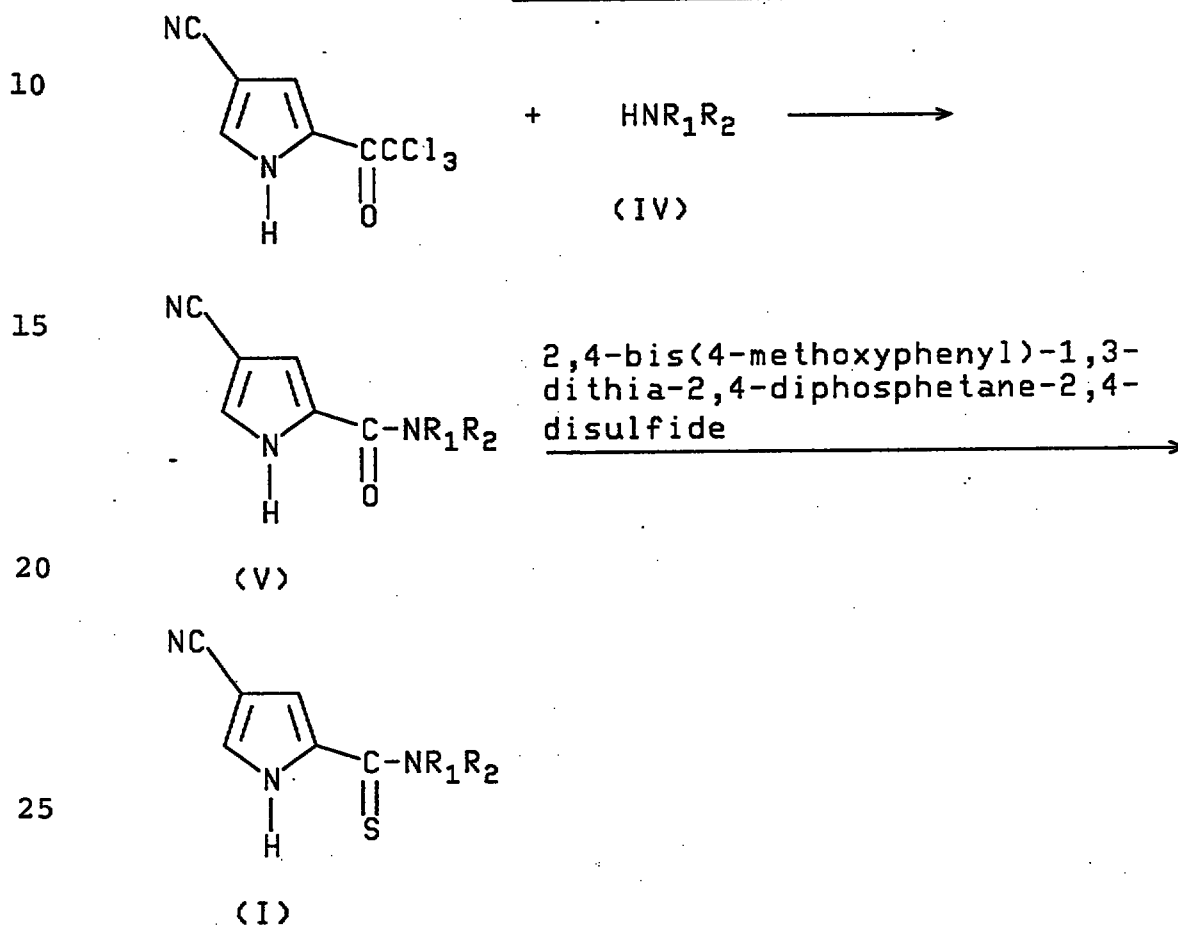
15 For example, wettable powders, dusts, and dust concentrate formulations can be prepared by grinding and blending together about 25% to about 85% by weight of formula I compounds and about 75% to about 15% by weight of a solid diluent such as bentonite, 20 diatomaceous earth, kaolin, attapulgite, or the like, about 1% to about 5% by weight of a dispersing agent such as sodium lignosulfonate, and about 1% to 5% by weight of a nonionic surfactant, such as octylphenoxy polyethoxy ethanol, nonylphenoxy polyethoxy ethanol or 25 the like.

30 A typical emulsifiable concentrate can be prepared by dissolving about 15% to about 70% by weight of a pyrrole thiocarboxamide compound in about 85% to about 30% by weight of a solvent such as isophorone, toluene, butyl cellosolve, methyl acetate, propylene glycol monomethyl ether, or the like and dispersing therein about 1% to 5% by weight of a nonionic surfactant such as an alkylphenoxy polyethoxy alcohol.



Certain formula I compounds of the invention wherein X is CN; Y, Z and R are hydrogen and W is as described above may be prepared as shown in Flow Diagram I.

5

FLOW DIAGRAM I

30

2-Trichloroacetylpyrrole-4-carbonitrile is reacted with at least about one molar equivalent of a formula IV amine compound to give a formula V 4-cyanopyrrole-2-carboxamide compound. The formula V intermediate is then reacted with at least about one molar

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equivalent of a reagent capable of introducing the thioxo group, such as 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, to give the desired 4-cyanopyrrole-2-thiocarboxamide of formula I.

Other insecticidal and acaricidal compounds of formula I may be prepared as shown in Flow Diagram II.

FLOW DIAGRAM II

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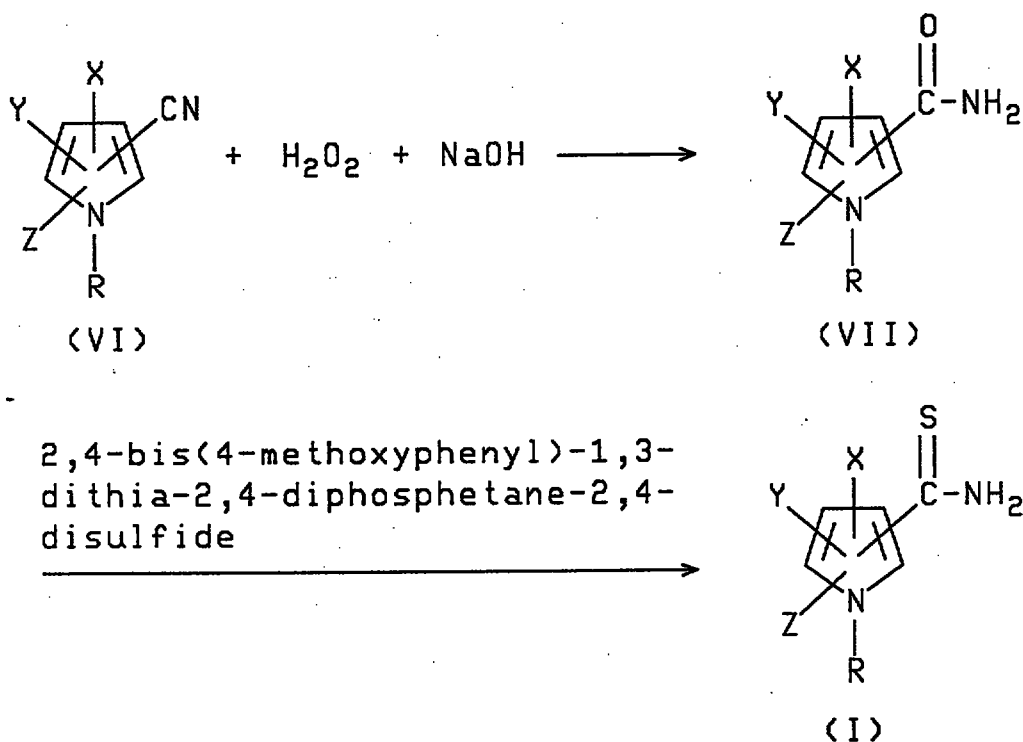
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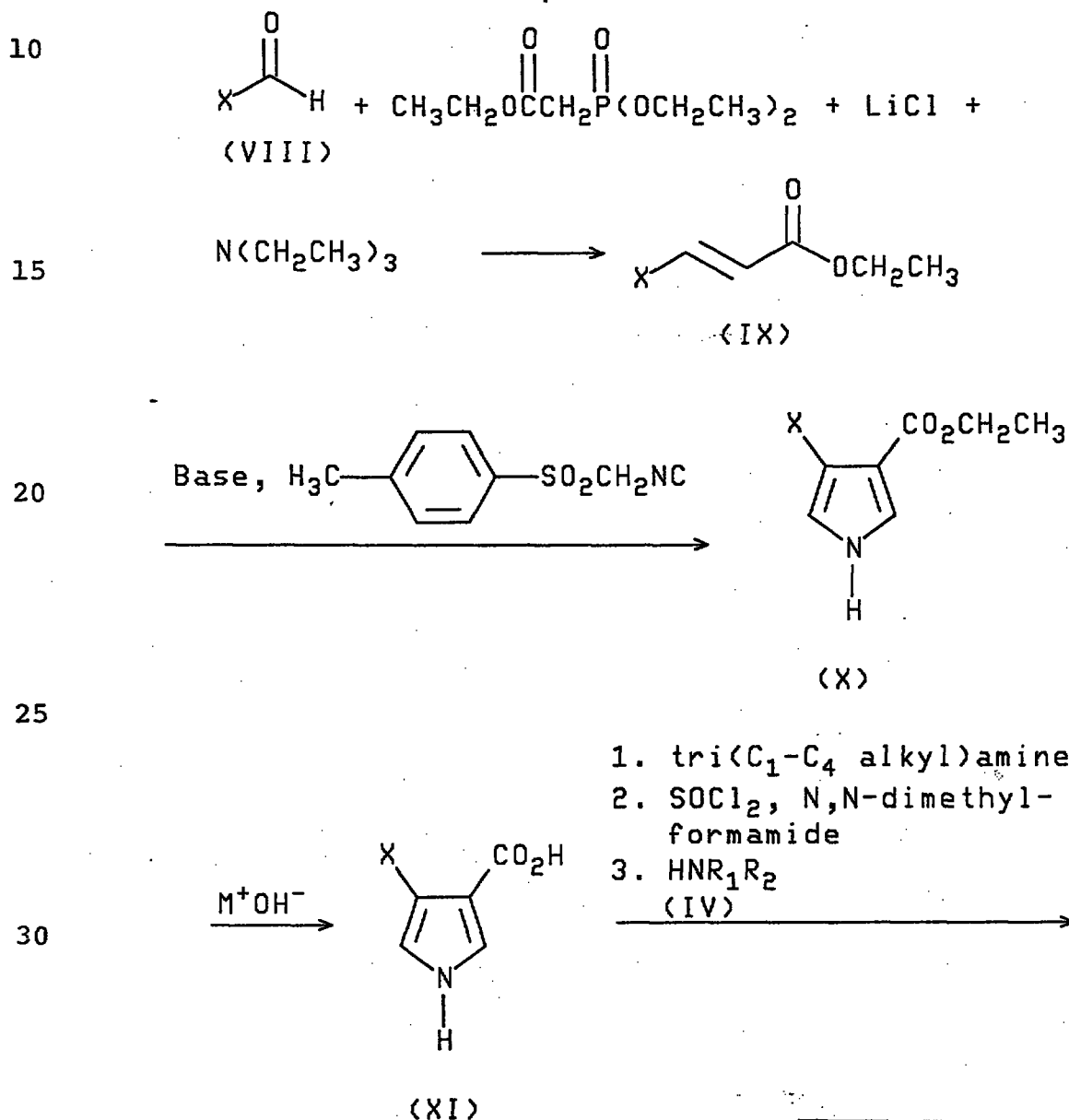


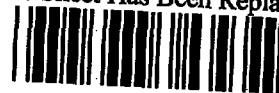
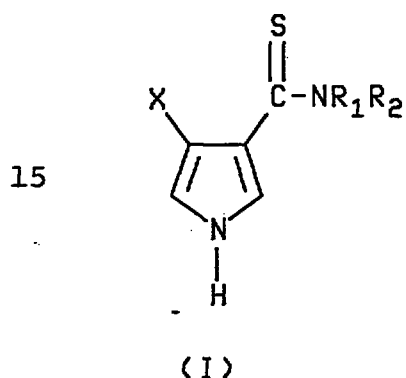
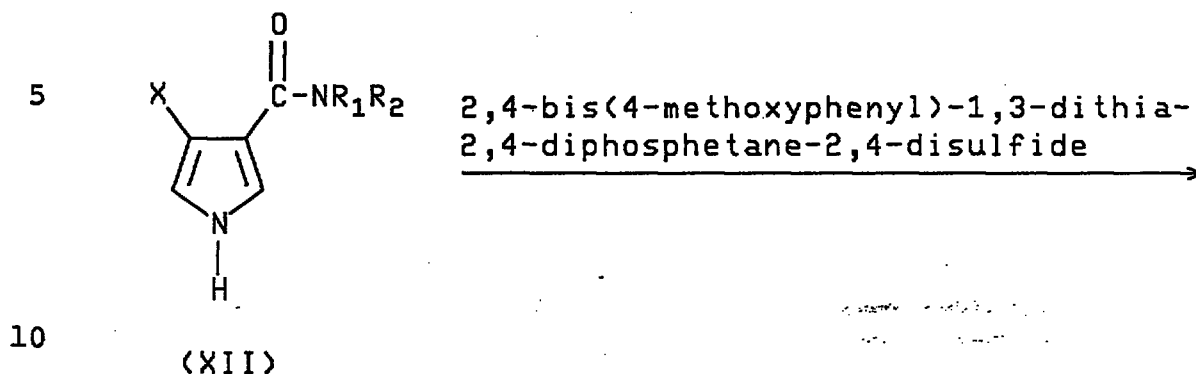
The appropriately substituted formula VI cyanopyrrole is reacted with an excess of hydrogen peroxide and sodium hydroxide to give the appropriately substituted formula VII pyrrole carboxamide. The intermediate formula VII compound is then reacted with at least about one molar equivalent of a reagent capable of introducing the thioxo group, such as 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-

2,4-disulfide, to give the appropriately substituted formula I pyrrole thiocarboxamide compound.

Certain insecticidal and acaricidal 4-(substituted phenyl)pyrrole-3-thiocarboxamide compounds of formula I may be prepared as shown in Flow Diagram III.

FLOW DIAGRAM III



FLOW DIAGRAM III (Continued)

wherein

X is Q or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

25 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

30 M is an alkali metal; and

Q, R₁ and R₂ are as described hereinabove for formula I.

35 The appropriately substituted formula VIII benzaldehyde is reacted with at least about one molar equivalent each of triethyl phosphonoacetate, lithium

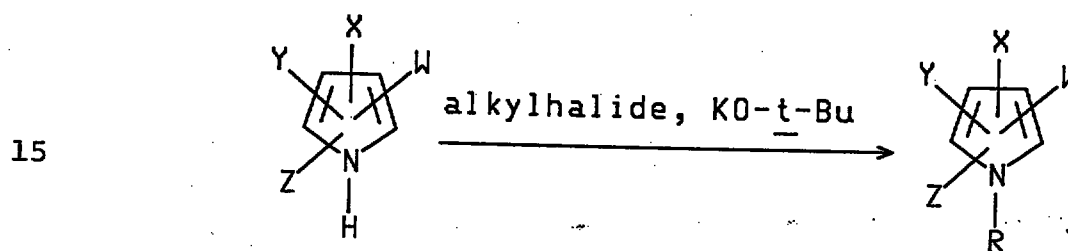


chloride and triethylamine to give the appropriately substituted ethyl cinnamate of formula IX. The formula IX cinnamate is reacted with at least about one molar equivalent of a strong base such as sodium hydride and at least about one molar equivalent of tosylmethyl isocyanide to give a formula X ethyl 4-(substituted phenyl)pyrrole-3-carboxylate which is hydrolyzed with an alkali metal hydroxide such as potassium hydroxide to give a formula XI 4-(substituted phenyl)pyrrole-3-carboxylic acid. The formula XI carboxylic acid is reacted with an excess of a tri(C₁-C₄ alkyl)amine to form a first mixture. The first mixture is reacted with an excess of thionyl chloride and at least about one molar equivalent of N,N-dimethylformamide to give a second mixture. The second mixture is reacted with an excess of a formula IV amine compound to give the formula XII 4-(substituted phenyl)pyrrole-3-carboxamide and reacting the formula XII carboxamide with a reagent capable of introducing the thio group, such as 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, to give the desired insecticidal and acaricidal 4-(substituted phenyl)pyrrole-3-thiocarboxamide of formula I.

Preparation of 1-substituted formula I pyrrole thiocarboxamide compounds can be achieved by reaction of the appropriately substituted formula I pyrrole thiocarboxamide having R as hydrogen with an alkylating or acylating agent in the presence of an alkali metal alkoxide or hydride. For example, a formula I pyrrole thiocarboxamide, wherein R is hydrogen and W, X, Y and Z are as described for formula I above, is reacted with an appropriate alkylating agent such as a C₁-C₆ alkylhalide in which the alkyl group is straight or branched and is optionally substituted with from one to three halogen atoms, one hydroxy, one



cyano, one C_1-C_4 alkoxy, one C_1-C_4 alkylthio, one phenyl group optionally substituted with from one to three halogen atoms, or one benzyloxy group optionally substituted with from one to three halogen atoms, and an alkali metal alkoxide such as sodium or potassium *t*-butoxide. This reaction provides a pyrrole thiocarboxamide having the same substituents as the starting material, but in addition is substituted on the nitrogen with a C_1-C_6 alkyl group optionally substituted as described above. This reaction may be illustrated as follows:



wherein W, X, Y and Z are as described for formula I above and R is C_1-C_6 alkyl optionally substituted as described above. In a similar reaction cyanogen bromide is substituted for the alkylhalide and yields the formula I pyrrole thiocarboxamide having a carbonitrile, rather than an alkyl group on the 1-position.

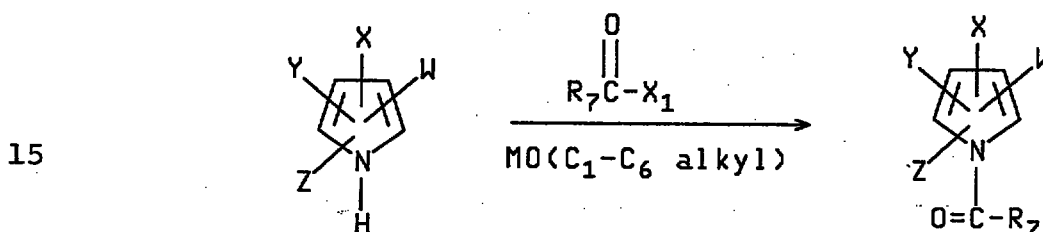
Advantageously, the above-described alkylation procedure of the formula I pyrrole thiocarboxamide compounds in which R is hydrogen may also be applied to the preparation of formula I pyrrole thiocarboxamides having an $N-C_3-C_6$ alkenyl or $N-C_3-C_6$ alkynyl substituent. This substitution is obtained by simply substituting a C_3-C_6 alkenyl halide or C_3-C_6 alkynyl halide for the C_1-C_6 alkyl halide in the above-described reaction.

In a similar manner, preparation of 1-acylated pyrrole thiocarboxamides may be achieved by the reaction of an appropriately substituted formula I



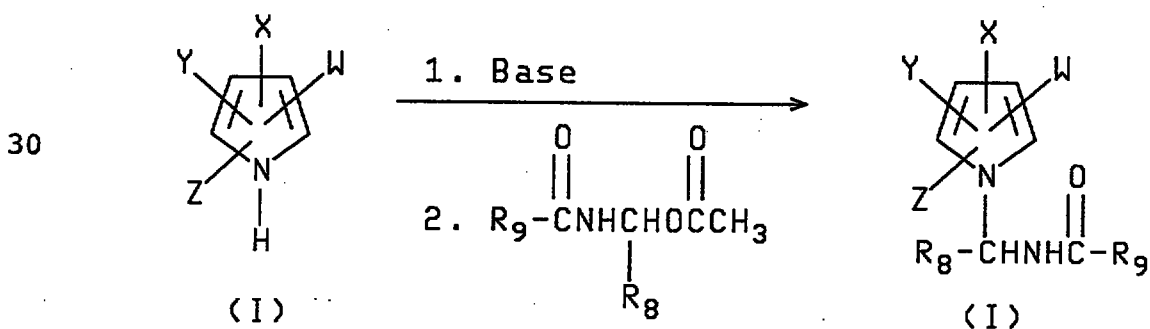
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pyrrole thiocarboxamide wherein R is hydrogen with an acylating agent in the presence of an alkali metal alkoxide. Acylating agents such as C₁-C₆ alkyl or C₂-C₆ alkenyl acid chlorides, substituted C₁-C₆ alkyl or C₂-C₆ alkenyl acid chlorides, benzoyl chloride, substituted benzoyl chlorides, phenylchloroformate, substituted phenylchloroformates, C₁-C₆ alkyl or C₂-C₆ alkenylchloroformates, substituted C₁-C₆ alkyl or C₂-C₆ alkenylchloroformates, N-substituted carbamoyl chlorides and the like may be employed. The reaction may be illustrated as follows:



wherein X₁ is halogen, M is an alkali metal and W, X, Y, Z and R₇ are as described hereinabove for formula I.

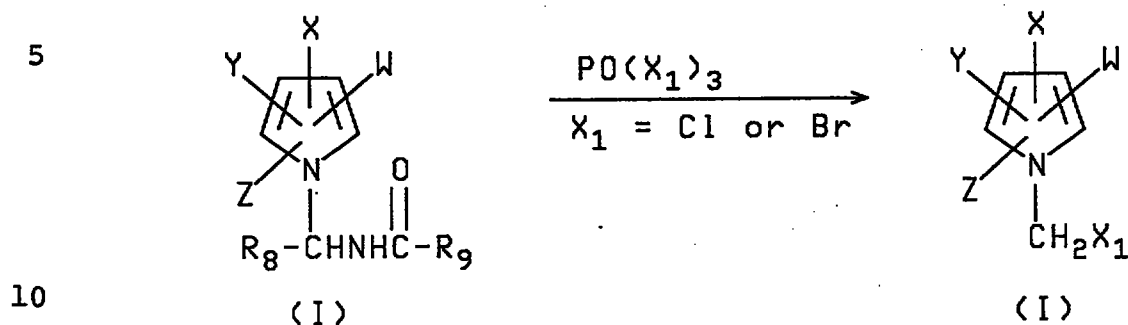
20 Formula I pyrrole thiocarboxamide compounds wherein R is CH₂SO₁ may be prepared by reaction of the appropriately substituted formula I pyrrole thiocarboxamide having A as chloromethyl with an alkali metal salt of an SO₁ compound in the presence of a base. And formula I pyrrole thiocarboxamide compounds wherein R is CHR₈NHC(O)R₉ may be prepared as shown below.



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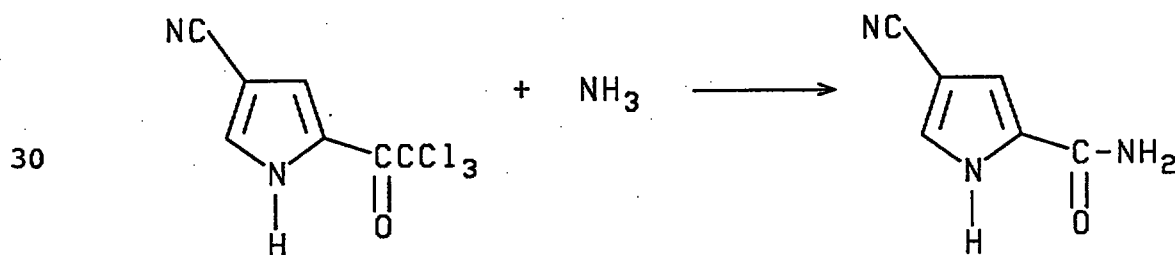
Advantageously, 1-halomethyl pyrrole thio-carboxamides of formula I may be prepared as shown below.



In order to facilitate a further understanding of the invention, the following examples are presented primarily for the purpose of illustrating more specific details thereof. The examples generally utilize the above reaction schemes and also provide further means for preparing even more compounds of the present invention which are not specifically described above. The invention should not be deemed limited by the examples as the full scope of the invention is defined in the claims.

EXAMPLE 1

25 Preparation of 4-Cyanopyrrole-2-carboxamide



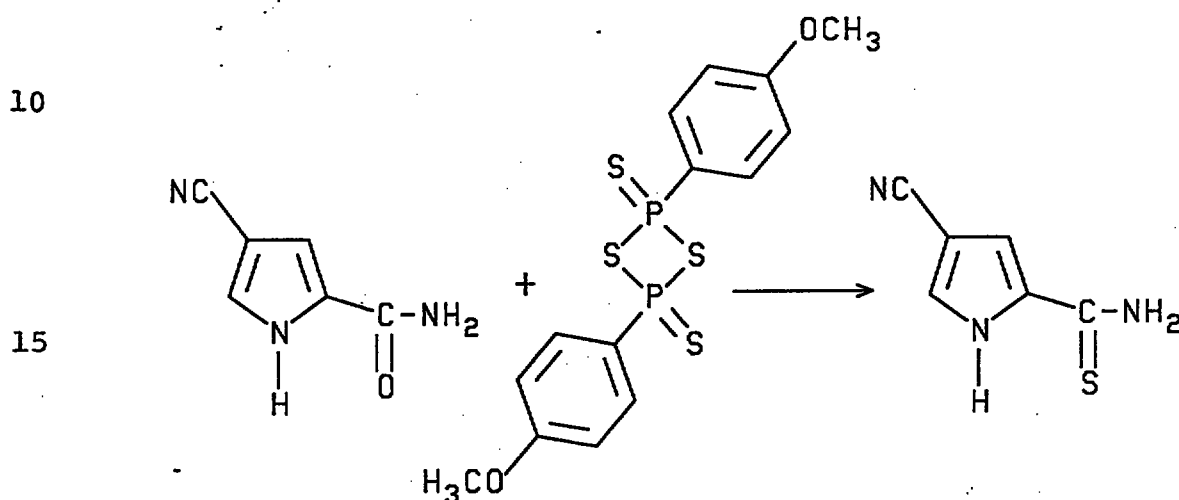
35 A solution of 2-trichloroacetylpyrrole-4-carbonitrile (20 g, 84.2 mmol) in methanol is treated

with ammonia (51 mL), stirred at room temperature for 30 minutes and diluted with water. The aqueous mixture is filtered to obtain the title product as a white solid (7.0 g, mp 253^o-256^oC).

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EXAMPLE 2

Preparation of 4-Cyanopyrrole-2-thiocarboxamide



20 A mixture of 4-cyanopyrrole-2-carboxamide (1.35 g, 10.0 mmol) and 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (4.0 g, 9.9 mmol) in toluene is heated at 100^oC for 4 1/2 hours, diluted with tetrahydrofuran and heated at reflux for

25 20 minutes. The reaction mixture is then cooled and concentrated in vacuo to obtain a residue. Chromatography of the residue using silica gel and a 4:1 hexanes/ethyl acetate mixture gives the title product as a yellow solid (0.9 g, mp 253^oC dec.).

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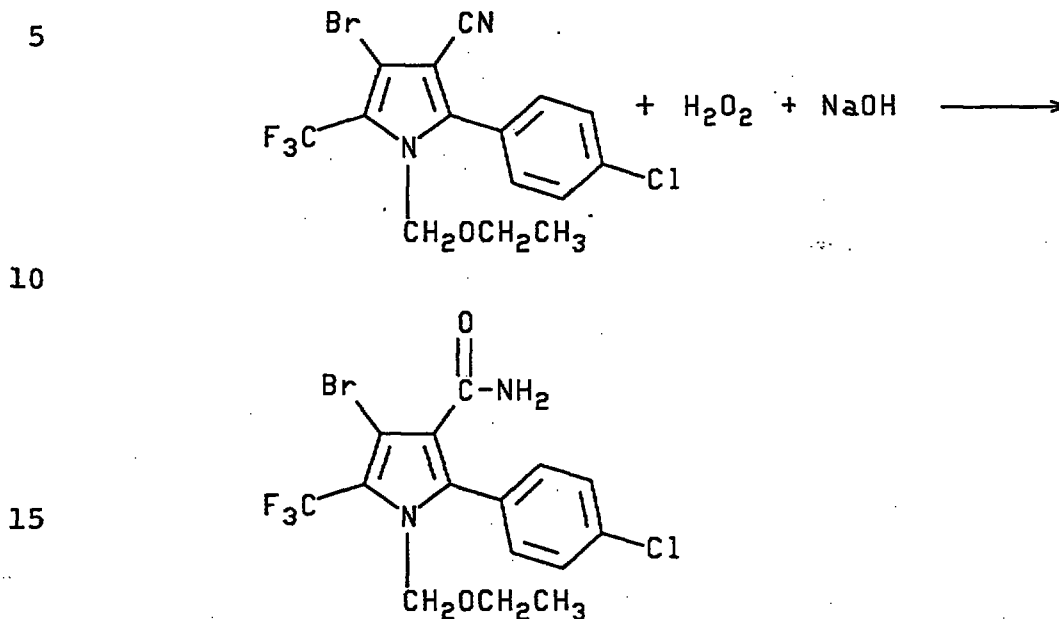
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EXAMPLE 3

Preparation of 4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxamide

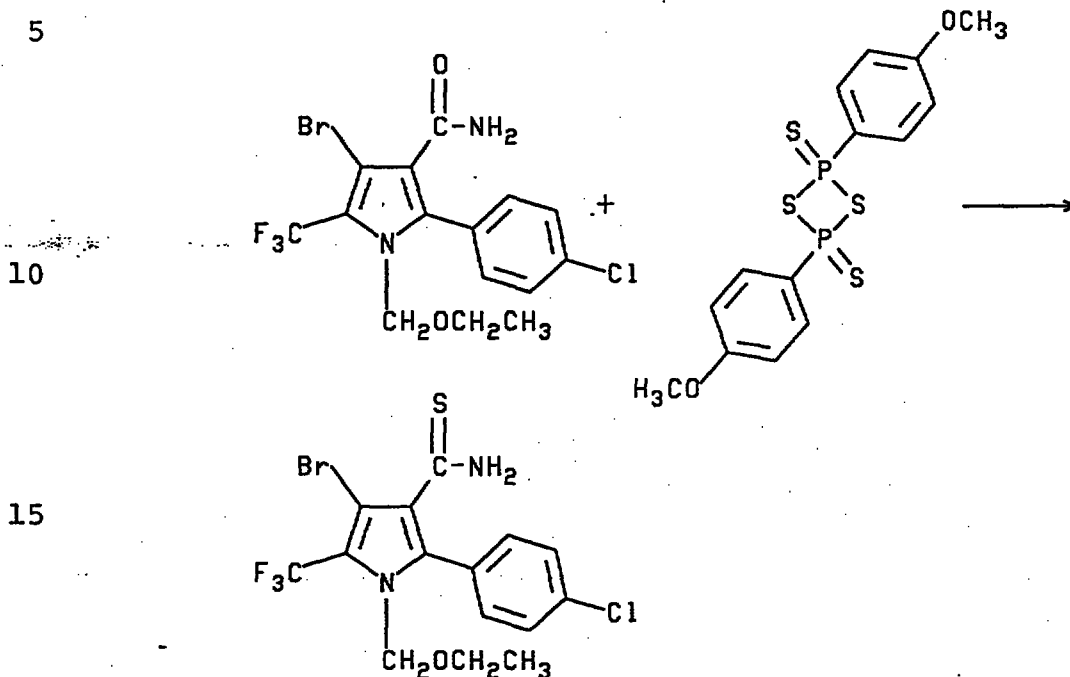


A mixture of 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (4.07 g, 10 mmol), sodium hydroxide (0.8 g, 20 mmol) and 30 wt/wt% hydrogen peroxide solution (7.2 mL, 70 mmol) in methanol is stirred at room temperature for 7 hours, treated with sodium hydroxide solution (0.8 g NaOH in 5 mL of H₂O) and 30 wt/wt% hydrogen peroxide solution (7 mL), stirred at room temperature overnight, heated at 40°C for 8 hours and diluted with water. The aqueous mixture is filtered and the filter cake is washed with water and heptane and dried to give the title product as a white solid (3.7 g) which is identified by ¹H and ¹³C NMR spectral analyses.



EXAMPLE 4

Preparation of 4-Bromo-2-(p-chlorophenyl)-1-ethoxymethyl-5-(trifluoromethyl)pyrrole-3-thiocarboxamide



20 A mixture of 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxamide (3.9 g, 9.2 mmol) and 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (5.7 g, 14.1 mmol) in acetonitrile is heated at reflux for 6 hours, cooled and concentrated in vacuo to obtain a residue.

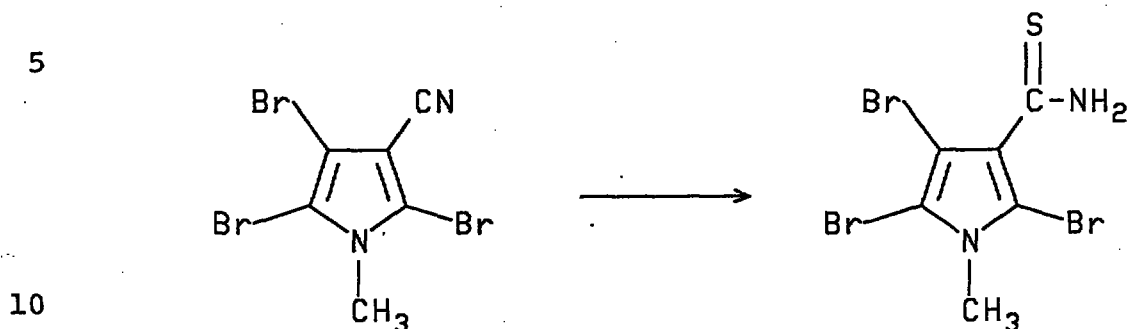
25 Chromatography of the residue using silica gel and a 4:1 hexanes/ethyl acetate mixture gives the title product as a yellow solid (1.5 g, mp 163°-172°C).

30



EXAMPLE 5

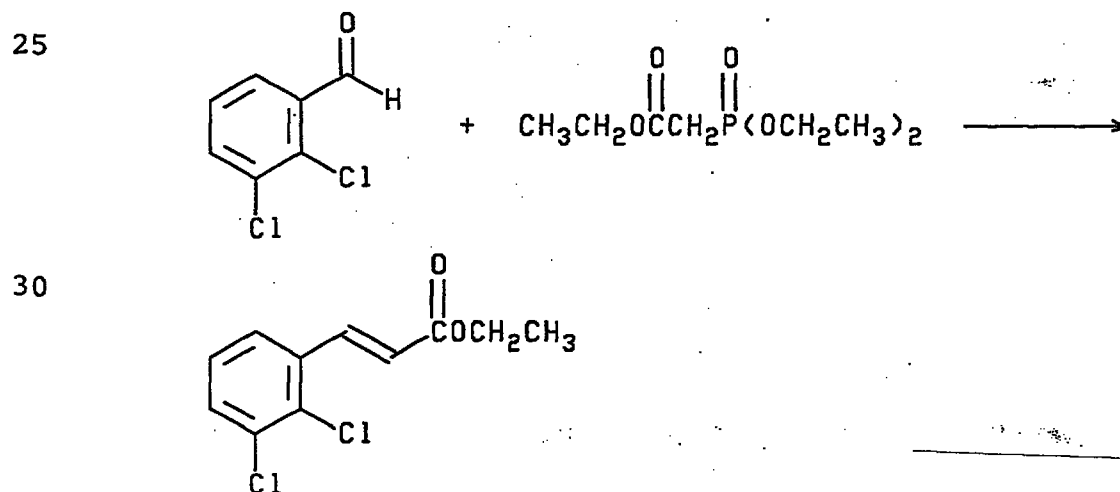
Preparation of 2,4,5-Tribromo-1-methylpyrrole-3-thio-carboxamide



Diisopropylethylamine (1.1 mL, 6 mmol), 2,4,5-tribromo-1-methylpyrrole-3-carbonitrile (2.16 g, 6 mmol) and pyridine (10 mL) are added to condensed hydrogen sulfide in a pressure tube at -78°C . The tube is sealed and the reaction mixture is stirred for 5 days at room temperature. The reaction mixture is then concentrated in vacuo to obtain a residue. Chromatography of the residue using silica gel and a 4:1 hexanes/ethyl acetate mixture gives the title product as a yellow solid (0.47 g, mp 100.5°C - 102°C dec.).

EXAMPLE 6

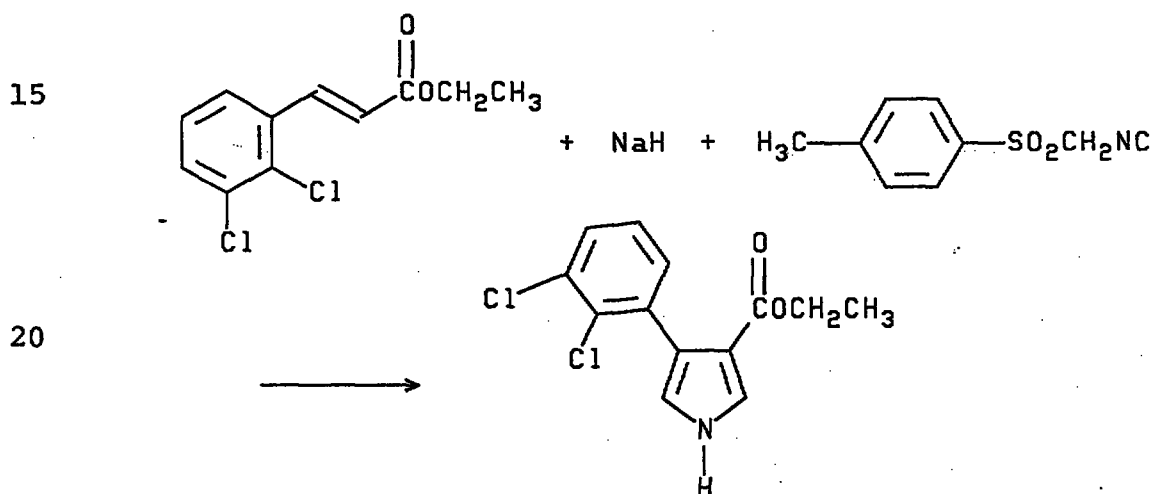
Preparation of Ethyl 2,3-dichlorocinnamate, (E)-





- 26 -

A mixture of 2,3-dichlorobenzaldehyde (17.5 g, 0.1 mol), triethyl phosphonoacetate (22.4 g, 0.12 mol), lithium chloride (5.1 g, 0.12 mol) and triethylamine (17 mL, 0.12 mol) in acetonitrile is stirred at room temperature for 1 hour and diluted with a water/ethyl acetate mixture. The organic phase is separated, washed with water dried over anhydrous Na_2SO_4 and concentrated in vacuo to give the title product as a yellow solid (42 g).

EXAMPLE 7**Preparation of Ethyl 4-(2,3-dichlorophenyl)pyrrole-3-carboxylate**

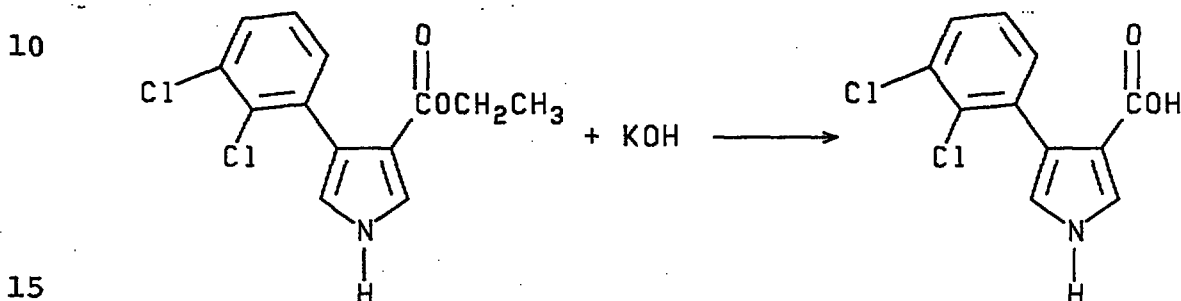
Sodium hydride (3.2 g, 60% in mineral oil) is washed with petroleum ether and suspended in tetrahydrofuran. A mixture of ethyl 2,3-dichlorocinnamate, (E)- (12.25 g, 50 mmol) and tosylmethyl isocyanide (11.7 g, 60 mmol) in tetrahydrofuran is added to the sodium hydride/tetrahydrofuran mixture. The reaction mixture is stirred for 1 hour, quenched with saturated ammonium chloride solution and extracted with diethyl ether. The organic extracts are combined, washed with water, dried over anhydrous Na_2SO_4 and concentrated in vacuo to obtain a residue. Chromatography of the

residue using silica gel and a 2:1 hexanes/ethyl acetate mixture gives the title product as a white solid (6.5 g) which is identified by ^1H and ^{13}C NMR spectral analyses.

5

EXAMPLE 8

Preparation of 4-(2,3-Dichlorophenyl)pyrrole-3-carboxylic acid



20

A mixture of ethyl 4-(2,3-dichlorophenyl)pyrrole-3-carboxylate (5.95 g, 21 mmol) and potassium hydroxide (6.5 g, 85%, 99 mmol) is heated at reflux for 6 hours, cooled, diluted with water and washed with diethyl ether. The aqueous phase is acidified with hydrochloric acid and filtered to obtain a solid. The solid is washed with diethyl ether and petroleum ether and dried to give the title product as a white solid

25

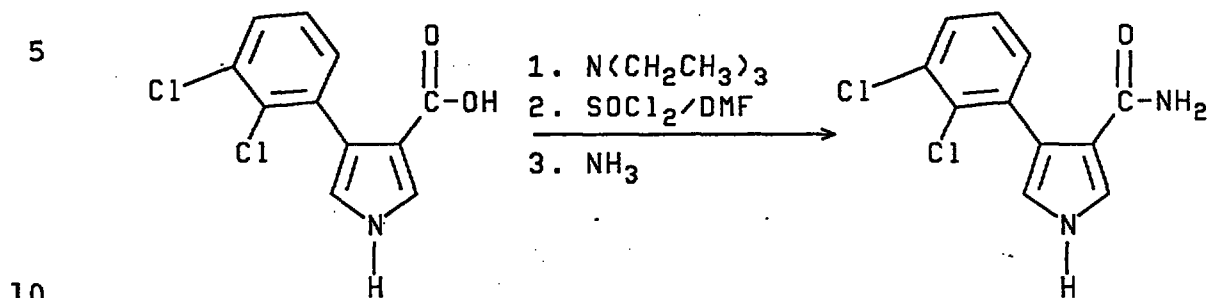
(5.24 g) which is identified by ^1H and ^{13}C NMR spectral analyses.

30



EXAMPLE 9

Preparation of 4-(2,3-Dichlorophenyl)pyrrole-3-carboxamide



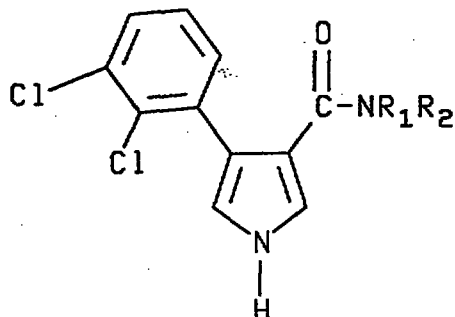
A mixture of 4-(2,3-dichlorophenyl)pyrrole-3-carboxylic acid (2.43 g, 9.5 mmol) and triethylamine (7 mL, 50 mmol) in tetrahydrofuran is stirred for 15 minutes at room temperature and concentrated in vacuo to obtain a residue. A mixture of the residue, thionyl chloride (2.77 mL, 38 mmol) and N,N-dimethylformamide (0.73 mL, 9.5 mmol) is stirred overnight at room temperature and concentrated in vacuo to obtain a yellow oil. The oil is added to a concentrated ammonia solution and stirred for 1 hour. This mixture is filtered to give a solid. The solid is washed with water, dried and chromatographed using silica gel and a 4:1 hexanes/ethyl acetate mixture to obtain the title product as a white solid (1.6 g, mp 185°-190°C).

Using essentially the same procedure, but substituting the appropriate amine for ammonia, the following compounds are obtained:

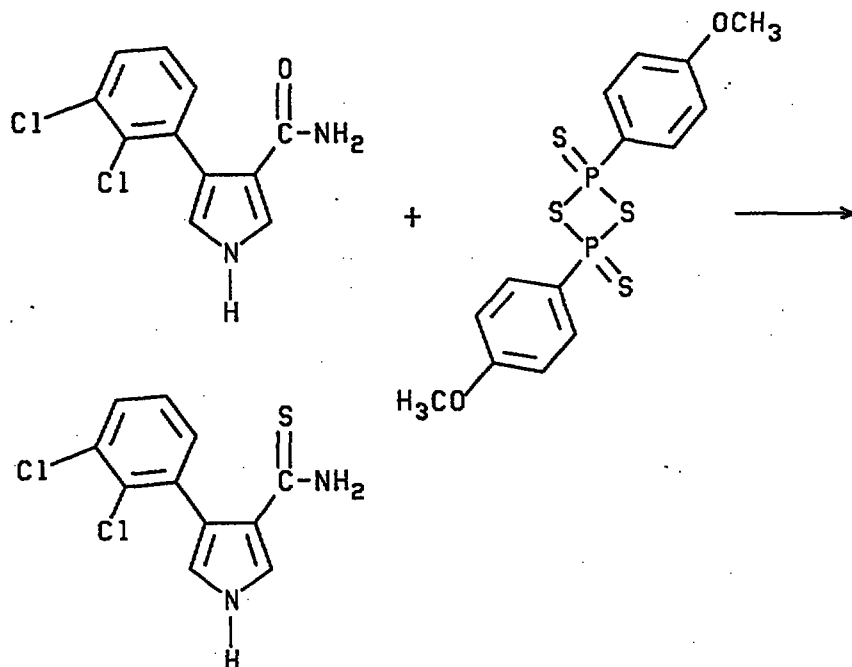




- 29 -



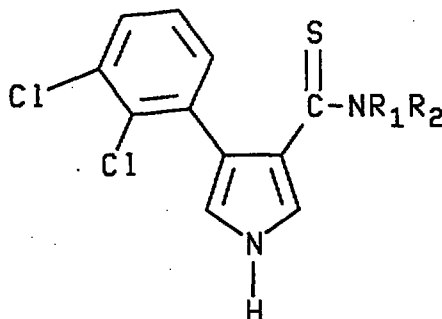
R_1	R_2	mp °C
H	CH ₃	134 - 137
CH ₃	CH ₃	133 - 136

EXAMPLE 10**Preparation of 4-(2,3-Dichlorophenyl)pyrrole-3-thio-**
carboxamide

A mixture of 4-(2,3-dichlorophenyl)pyrrole-3-carboxamide (0.98 g, 3.8 mmol) and 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (0.77 g, 1.9 mmol) in tetrahydrofuran is heated at

reflux for 75 minutes, cooled and concentrated in vacuo to obtain a residue. Chromatography of the residue using silica gel and a 1:1 hexane/ethyl acetate mixture gives the title product as a yellow solid (0.54 g, mp 128°-132°C).

Using essentially the same procedure, but using the appropriately substituted pyrrole carboxylic amide, the following compounds are obtained:



$\frac{R_1}{H}$
 $\frac{CH_3}{CH_3}$

$\frac{R_2}{CH_3}$
 $\frac{CH_3}{CH_3}$

$\frac{mp^\circ C}{158 - 162}$
 $\frac{226 - 229}{226 - 229}$

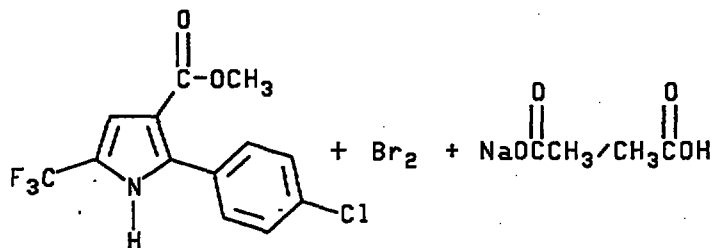
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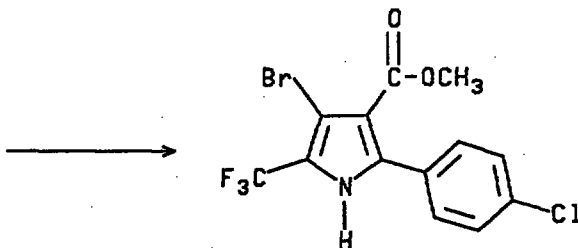
EXAMPLE 11

Preparation of Methyl 4-bromo-2-(p-chlorophenyl)-5-(trifluoromethyl)pyrrole-3-carboxylate

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Bromine (2.3 mL, 43.7 mmol) is added to a solution of methyl 2-(p-chlorophenyl)-5-(trifluoromethyl)pyrrole-3-carboxylate (8.44 g, 29.2 mmol) and sodium acetate (3.6 g, 43.7 mmol) in acetic acid. The reaction mixture is stirred for 30 minutes, diluted with a 0.4 wt/wt% sodium sulfite solution and extracted with diethyl ether. The organic extracts are combined, washed with saturated sodium hydrogen carbonate solution, dried over anhydrous Na₂SO₄ and concentrated in vacuo to obtain an oil which solidifies to give the title product as a solid (9.2 g) which is identified by ¹H and ¹³C NMR spectral analyses.

20

25

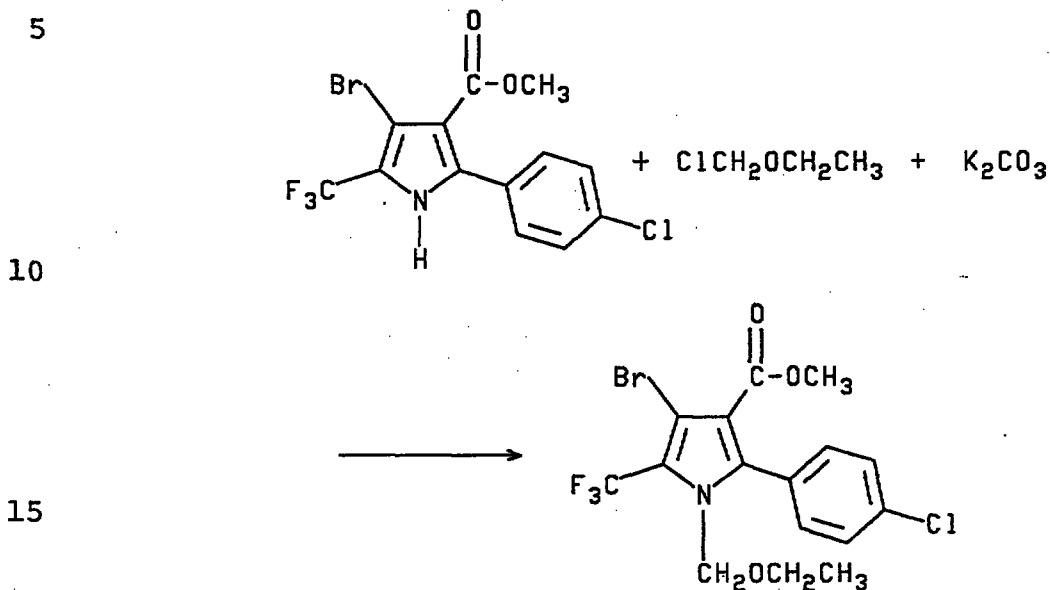
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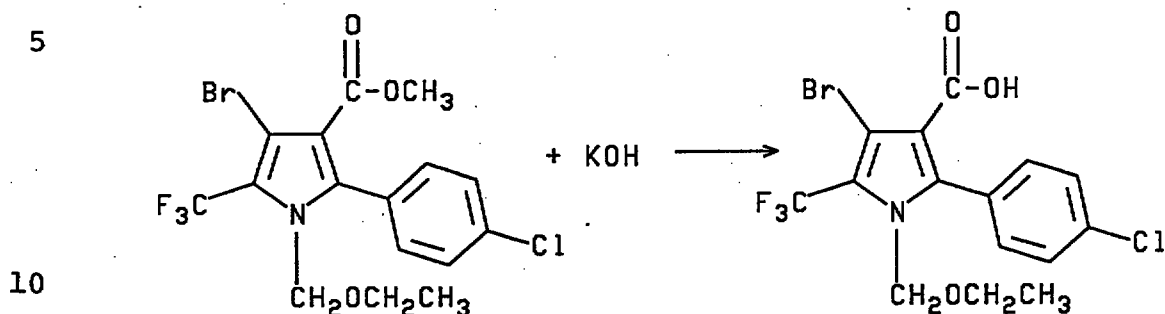
EXAMPLE 12

Preparation of Methyl 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxylate



A mixture of methyl 4-bromo-2-(p-chloro-phenyl)-5-(trifluoromethyl)pyrrole-3-carboxylate (9.2 g, 24.1 mmol), potassium carbonate (4.96 g, 36 mmol) and chloromethyl ethyl ether (3.3 mL, 36 mmol) is stirred at room temperature for 21 hours, treated with potassium carbonate (4.9 g) and chloromethyl ethyl ether (3.3 mL), stirred for 1 hour, treated with potassium carbonate (4.9 g) and chloromethyl ethyl ether (3.3 mL) stirred for 3 hours, diluted with water and extracted with diethyl ether. The combined organic extracts are washed with water, dried over anhydrous MgSO_4 and concentrated in vacuo to obtain the title product as a brown oil (13.1 g) which is used in the next step without further purification.

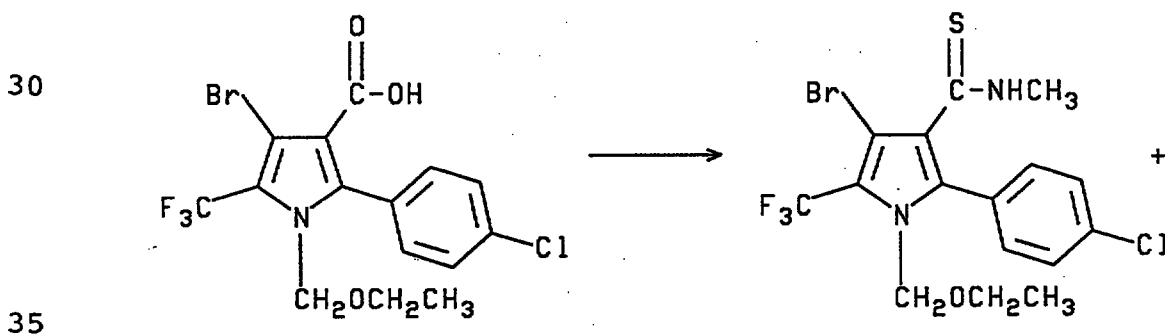


**EXAMPLE 13****Preparation of 4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxylic acid**

A mixture of methyl 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxylate (13.1 g) and potassium hydroxide (3.12 g, 85%, 48 mmol) is stirred at room temperature for 20 hours, stirred at reflux for 2 hours, diluted with water, washed with diethyl ether, acidified to pH 4 with 1N hydrochloric acid and filtered to obtain a solid. The solid is washed with water and petroleum ether and dried to give the title product as a white solid (6.45 g) which is identified by ^1H NMR spectral analysis.

EXAMPLE 14

25 **Preparation of 4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N-methyl-5-(trifluoromethyl)pyrrole-3-thio-carboxamide**





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Isobutylchloroformate (0.3 mL, 2.3 mmol) is added to a mixture of 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxylic acid (0.83 g, 2 mmol) and triethylamine (0.33 mL, 2.3 mmol) in tetrahydrofuran at 0°C. The mixture is stirred for 1 hour at 0°C, treated with a 6 wt/wt% methylamine solution (10.6 g, 20 mmol), stirred at room temperature for 2 hours and diluted with a diethyl ether/water mixture. The organic phase is separated, dried over anhydrous Na₂SO₄, concentrated in vacuo, diluted with toluene and concentrated in vacuo to obtain a liquid. A mixture of the liquid in tetrahydrofuran is treated with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (0.40 g, 1 mmol), heated at reflux for 2 hours, concentrated in vacuo and chromatographed on silica gel with a 4:1 hexane/ethyl acetate mixture to obtain the title product as a yellow gum (0.3 g) which is identified by ¹H and ¹³C NMR spectral analyses.

Using essentially the same procedure, but substituting dimethylamine for methylamine, 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N,N-dimethyl-5-(trifluoromethyl)pyrrole-3-thiocarboxamide is obtained as a yellow gum.

EXAMPLE 15

Insecticide and acaricide evaluations

The following tests show the efficacy of the compounds as insecticides and acarides. The evaluations are conducted with solutions of test compounds dissolved or dispersed in 50/50 acetone/water mixtures. The test compound is technical material dissolved or dispersed in said acetone/water mixtures in sufficient amount to provide the concentrations set forth in Table I below.



All concentrations reported herein are in terms of active ingredient. All tests are conducted in a laboratory maintained at about 27°C. The rating system employed is as follows:

5

Rating System

10	0 = no effect	5 = 56-65% kill
	1 = 10-25% kill	6 = 66-75% kill
	2 = 26-35% kill	7 = 76-85% kill
	3 = 36-45% kill	8 = 86-99% kill
	4 = 46-55% kill	9 = 100% kill
		- = not evaluated

15 The test species of insects used in the present evaluations along with specific test procedures are described below.

Spodoptera eridania 3rd instar larvae, southern army-worm

20 A sieva lima bean leaf expanded to 7 to 8 cm in length is dipped in the test suspension with agitation for 3 seconds and placed in a hood to dry. The leaf is then placed in a 100x10 mm petri dish containing a damp filter paper on the bottom and 10 3rd instar caterpillars. The dish is maintained for 5 days before
25 observations are made of mortality, reduced feeding, or any interference with normal moulting.

Tetranychus urticae (OP-resistant strain), 2-spotted spider mite

30 Sieva lima bean plants with primary leaves expanded to 7 to 8 cm are selected and cut back to one plant per pot. A small piece is cut from a leaf taken from the main colony and placed on each leaf of the
35 test plants. This is done about 2 hours before



treatment to allow the mites to move over to the test plant and to lay eggs. The size of the cut piece is varied to obtain about 100 mites per leaf. At the time of the treatment, the piece of leaf used to transfer the mites is removed and discarded. The mite-infested plants are dipped in the test formulation for 3 seconds with agitation and set in the hood to dry. Plants are kept for 2 days before estimates of adult kill are made.

Heliothis virescens, 3rd instar tobacco budworm

Cotton cotyledons are dipped in the test formulation and allowed to dry in a hood. When dry, each is cut into quarters and ten sections placed individually in 30 mL plastic medicine cups containing a 5 to 7 mm long piece of damp dental wick. One 3rd instar caterpillar is added to each cup and a cardboard lid is placed on the cup. Treatments are maintained for 3 days before mortality counts and estimates of reduction in feeding damage are made.

Dibrotia undecimpunctata howardi, 3rd instar southern corn rootworm

One cc of fine talc is placed in a 30 mL wide-mouth screw-top glass jar. One mL of the appropriate acetone test solution is pipetted onto the talc so as to provide 1.25 mg and 0.25 mg of active ingredient per jar. The jars are set under a gentle air flow until the acetone is evaporated. The dried talc is loosened, 1 cc of millet seed is added to serve as food for the insects and 25 mL of moist soil is added to each jar. The jars are capped and contents thoroughly mixed on a Vortex Mixer. Following this, ten 3rd instar rootworms are added to each jar and the jars are loosely capped to allow air exchange for the

larvae. The treatments are held for 6 days before mortality counts are made. Missing larvae are presumed dead, since they decompose rapidly and can not be found. The concentrations used in this test correspond
5 approximately to 50 kg/ha and 10 kg/ha, respectively.

The data obtained for the above described evaluations are reported in Table I.

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TABLE I

Insecticide and Acaricide Evaluations

Compound	OP.					
	Resistant		Tobacco		Southern Corn	
	Armyworm	Mites	Budworm	Budworm	Rootworm	Rootworm
	(ppm)	(ppm)	(ppm)	(ppm)	(kg/ha)	(kg/ha)
	1000	300	100	100	50	10
4-Cyanopyrrole-2-thiocarbonyl xamide	9	0	-	-	9	-
4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-thiocarbonyl xamide	9	9	9	9	9	9
4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N-methyl-5-(trifluoromethyl)pyrrole-3-thiocarbonyl xamide	-	3	-	-	-	-

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TABLE I (Continued)

Compound	OP.							
	Armyworm		Resistant Mites		Tobacco Budworm		Southern Corn Rootworm	
	(ppm)		(ppm)		(ppm)		(kg/ha)	
	1000	100	10	300	100	100	50	10

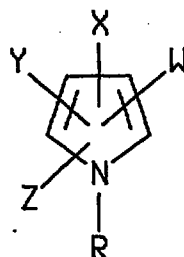
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I CLAIM:

1. A compound having the structural formula



wherein

W is $\text{C}(\text{S})\text{NR}_1\text{R}_2$;

R_1 and R_2 are each independently hydrogen,

C_1 - C_4 alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;

X is Cl, Br, CN, NO_2 , Q,

C_1 - C_4 alkyl substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

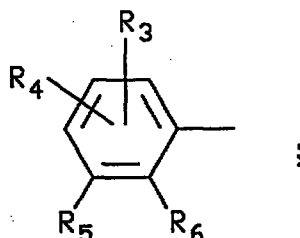
C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;





Q is



R_3 and R_4 are each independently hydrogen, halogen, NO_2 , CN or $\text{C}_1\text{-C}_4$ alkyl optionally substituted with one or more halogen atoms;

R_5 and R_6 are taken together with the atoms to which they are attached to form a 5- or 6-membered heterocyclic ring containing 1 or 2 oxygen atoms and optionally substituted with one or more halogen atoms or $\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms;

Y is hydrogen, Cl, Br, CN, NO_2 , $\text{S(O)}_n\text{T}$, Q,

$\text{C}_1\text{-C}_4$ alkyl substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or

$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, Cl, Br, $\text{S(O)}_n\text{T}$ or $\text{C}_1\text{-C}_4$ alkyl substituted with one or more halogen atoms;

T is $\text{C}_1\text{-C}_4$ alkyl substituted with one or more halogen atoms;

n is an integer of 0, 1 or 2;

R is A, OA or CN;

A is hydrogen, CR_7 , $\text{CHR}_8\text{NHCOR}_9$, CH_2SO_1 ,





- C_1-C_6 alkyl optionally substituted with one to three halogen atoms,
one tri(C_1-C_4 alkyl)silyl,
one hydroxy,
one cyano,
one or two C_1-C_4 alkoxy groups optionally substituted with one to three halogen atoms,
one C_1-C_4 alkylthio,
one phenyl optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
one phenoxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
one C_1-C_6 alkoxycarbonyl group optionally





substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or

one benzylcarbonyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

C_3-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group, or

C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group;

R_7 is C_1-C_6 alkyl or C_3-C_6 cycloalkyl each optionally substituted with one to three halogen atoms, one hydroxy, one cyano,

one or two C_1-C_4 alkoxy groups optionally substituted with one to three halogen atoms,

one C_1-C_4 alkylthio,

one phenyl group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

one phenoxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

one C_1-C_6 alkylcarbonyloxy group optionally





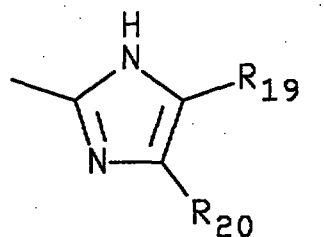
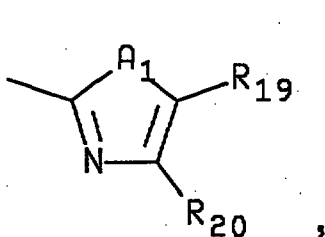
substituted with one to three halogen atoms,
one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
one C_1-C_6 alkoxy carbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or
one benzyloxycarbonyl group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
 C_2-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group,
 C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group,
phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, phenoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,
phenoxy optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,





1- or 2-naphthyl,
 2-, 3-, or 4-pyridyl optionally substituted with
 one to three halogen atoms,
 C_1-C_6 alkoxy optionally substituted with one to
 three halogen atoms, or
 C_2-C_6 alkenyloxy optionally substituted with one
 to three halogen atoms;
 R_8 is hydrogen or C_1-C_4 alkyl;
 R_9 is C_1-C_6 alkyl optionally substituted with one to
 three halogen atoms,
 phenyl optionally substituted with one to three
 halogen atoms, CN groups, NO_2 groups, C_1-C_4
 alkyl groups, C_1-C_4 alkoxy groups or CF_3
 groups,
 2- or 3-thienyl, or
 2- or 3-furyl;

Q_1 is $\begin{array}{c} A_1 \\ || \\ C-R_{10} \end{array}$, $\begin{array}{c} A_1 \\ || \\ C-OR_{11} \end{array}$, $\begin{array}{c} A_1 \\ || \\ C-NR_{12}R_{13} \end{array}$, $\begin{array}{c} A_1 \\ || \\ P(OR_{14})_2 \end{array}$, $\begin{array}{c} NR_{15} \\ || \\ C-NR_{16}R_{17} \end{array}$,
 $\begin{array}{c} NR_{15} \\ || \\ C-A_1R_{18} \end{array}$,



CN,

C_1-C_6 alkyl optionally substituted with one or
 more halogen atoms, CN groups or phenyl
 groups, or
 phenyl optionally substituted with one or more
 halogen atoms, C_1-C_4 alkyl groups, C_1-C_4
 alkoxy groups, CN groups, NO_2 groups, CF_3
 groups or $NR_{21}R_{22}$ groups;

A_1 is O or S;





- R_{10} is C_1-C_6 alkyl or phenyl;
 R_{11} is C_1-C_6 alkyl;
 R_{12} and R_{13} are each independently hydrogen, C_1-C_6 alkyl or may be taken together with the atom to which they are attached to form a 5- to 7-membered ring;
 R_{14} is C_1-C_4 alkyl;
 R_{15} is hydrogen, C_1-C_4 alkyl or may be taken together with either R_{16} or R_{18} and the atoms to which they are attached to form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;
 R_{16} and R_{17} are each independently hydrogen or C_1-C_4 alkyl;
 R_{18} is C_1-C_4 alkyl or when taken together with R_{15} and the atoms to which they are attached may form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;
 R_{19} and R_{20} are each independently hydrogen or C_1-C_4 alkyl or when taken together may form a ring wherein $R_{19}R_{20}$ is represented by $-CH=CH-CH=CH-$; and
 R_{21} and R_{22} are each independently hydrogen or C_1-C_4 alkyl;

with the proviso that when W is on the 3-position of the pyrrole ring, X is on the 4-position of the pyrrole ring, and Y, Z and R are each hydrogen, then X is other than 2- or 3-chlorophenyl; and with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H; and with the further proviso that when R_1 and R_2 are both H, then X and Y are other than phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,



C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms.

2. The compound according to claim 1
wherein

$\begin{array}{c} S \\ || \\ W \text{ is } CNR_1R_2; \end{array}$

R_1 and R_2 are each independently hydrogen or C_1-C_4 alkyl;

X is Q or phenyl optionally substituted with one or more halogen atoms,

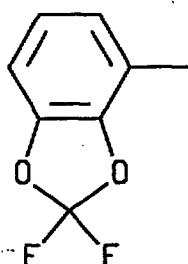
NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Q is



Y is hydrogen, Cl , Br , CN , NO_2 or CF_3 ;

Z is hydrogen, Cl , Br or CF_3 ;

R is A or CN ;

$\begin{array}{c} O \\ || \\ A \text{ is hydrogen, } CR_7 \text{ or} \end{array}$

C_1-C_6 alkyl optionally substituted with one to three halogen atoms,
one C_1-C_4 alkoxy group,

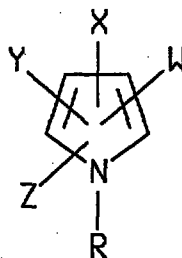




one cyano,
 one C₁-C₆ alkylcarbonyloxy group,
 one benzylcarbonyloxy group, or
 one phenylcarbonyloxy group optionally substituted with one to three halogen atoms or one C₁-C₄ alkyl group; and
 R₇ is phenyl optionally substituted with one or more halogen atoms, C₁-C₄ alkyl groups, C₁-C₄ alkoxy groups, CN groups, NO₂ groups or CF₃ groups.

3. The compound according to claim 2 selected from the group consisting of 4-cyanopyrrole-2-thiocarboxamide; 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-thiocarboxamide; 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N-methyl-5-(trifluoromethyl)pyrrole-3-thiocarboxamide; and 4-(2,3-dichlorophenyl)pyrrole-3-thiocarboxamide.

4. A method for controlling insects and acarina which comprises contacting said insects and acarina, their breeding grounds, food supply or habitat with an insecticidally or acaricidally effective amount of a compound having the structural formula



wherein

S
 ||
 W is CNR₁R₂;

R₁ and R₂ are each independently hydrogen, C₁-C₄ alkyl optionally substituted with one or





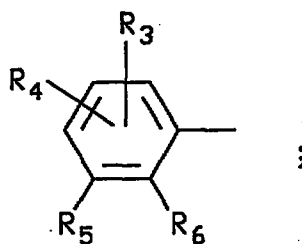
phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

X is Cl, Br, CN, NO₂, Q,

C₁-C₄ alkyl substituted with one or more halogen
atoms, or

phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

Q is



R₃ and R₄ are each independently hydrogen, halogen,
NO₂, CN or C₁-C₄ alkyl optionally substituted with
one or more halogen atoms;

R₅ and R₆ are taken together with the atoms to which
they are attached to form a 5- or 6-membered
heterocyclic ring containing 1 or 2 oxygen atoms
and optionally substituted with one or more
halogen atoms or C₁-C₄ alkyl groups optionally
substituted with one or more halogen atoms;



Y is hydrogen, Cl, Br, CN, NO₂, S(O)_nT, Q,
C₁-C₄ alkyl substituted with one or more halogen
atoms, or

phenyl optionally substituted with one or more
halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

Z is hydrogen, Cl, Br, S(O)_nT or C₁-C₄ alkyl substi-
tuted with one or more halogen atoms;

T is C₁-C₄ alkyl substituted with one or more halogen
atoms;

n is an integer of 0, 1 or 2;

R is A, OA or CN;

A is hydrogen, $\overset{\text{O}}{\parallel}\text{CR}_7$, $\text{CHR}_8\overset{\text{O}}{\parallel}\text{NCR}_9$, CH₂SO₁,
C₁-C₆ alkyl optionally substituted with one to
three halogen atoms,
one tri(C₁-C₄ alkyl)silyl,
one hydroxy,
one cyano,
one or two C₁-C₄ alkoxy groups optionally
substituted with one to three halogen
atoms,
one C₁-C₄ alkylthio,
one phenyl optionally substituted with one to
three halogen atoms, one to three C₁-C₄
alkyl groups or one to three C₁-C₄
alkoxy groups,
one phenoxy group optionally substituted with



one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,

one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,

one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

one C_1-C_6 alkoxycarbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or

one benzylcarbonyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

C_3-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group, or

C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group;

R_7 is C_1-C_6 alkyl or C_3-C_6 cycloalkyl each optionally substituted with one to three halogen atoms,

one hydroxy,

one cyano,





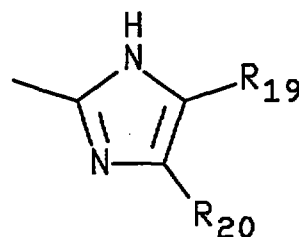
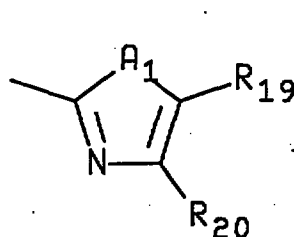
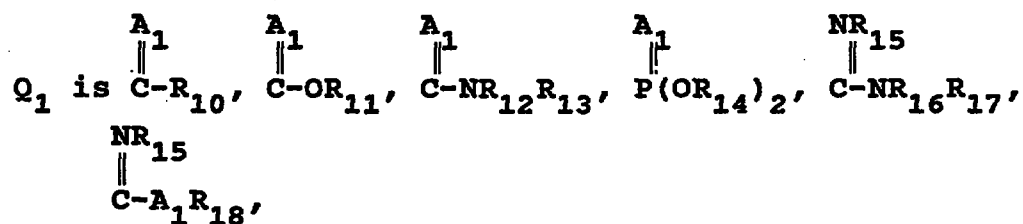
- one or two C_1-C_4 alkoxy groups optionally substituted with one to three halogen atoms,
- one C_1-C_4 alkylthio,
- one phenyl group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one phenoxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
- one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
- one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one C_1-C_6 alkoxycarbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or
- one benzyloxycarbonyl group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4





alkyl groups or one to three C_1-C_4 alkoxy groups,
 C_2-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group,
 C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group,
phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, phenoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,
phenoxy optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,
1- or 2-naphthyl,
2-, 3-, or 4-pyridyl optionally substituted with one to three halogen atoms,
 C_1-C_6 alkoxy optionally substituted with one to three halogen atoms, or
 C_2-C_6 alkenyloxy optionally substituted with one to three halogen atoms;
 R_8 is hydrogen or C_1-C_4 alkyl;
 R_9 is C_1-C_6 alkyl optionally substituted with one to three halogen atoms,
phenyl optionally substituted with one to three halogen atoms, CN groups, NO_2 groups, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups or CF_3 groups,
2- or 3-thienyl, or
2- or 3-furyl;





CN,

C_1-C_6 alkyl optionally substituted with one or more halogen atoms, CN groups or phenyl groups, or

phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO_2 groups, CF_3 groups or $NR_{21}R_{22}$ groups;

A_1 is O or S;

R_{10} is C_1-C_6 alkyl or phenyl;

R_{11} is C_1-C_6 alkyl;

R_{12} and R_{13} are each independently hydrogen, C_1-C_6 alkyl or may be taken together with the atom to which they are attached to form a 5- to 7-membered ring;

R_{14} is C_1-C_4 alkyl;

R_{15} is hydrogen, C_1-C_4 alkyl or may be taken together with either R_{16} or R_{18} and the atoms to which they are attached to form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

R_{16} and R_{17} are each independently hydrogen or C_1-C_4 alkyl;

R_{18} is C_1-C_4 alkyl or when taken together with R_{15} and





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the atoms to which they are attached may form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

R_{19} and R_{20} are each independently hydrogen or C_1-C_4 alkyl or when taken together may form a ring wherein $R_{19}R_{20}$ is represented by $-CH=CH-CH=CH-$; and

R_{21} and R_{22} are each independently hydrogen or C_1-C_4 alkyl;

with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.

5. The method according to claim 4

wherein

$\begin{array}{c} S \\ || \\ W \end{array}$ is CNR_1R_2 ;

R_1 and R_2 are each independently hydrogen or C_1-C_4 alkyl;

X is Q or phenyl optionally substituted with one or more halogen atoms,

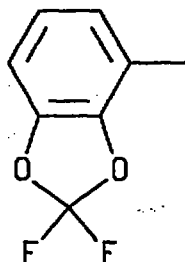
NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Q is



;





Y is hydrogen, Cl, Br, CN, NO₂ or CF₃;

Z is hydrogen, Cl, Br or CF₃;

R is A or CN;

A is hydrogen, $\overset{\text{O}}{\parallel}\text{CR}_7$ or

C₁-C₆ alkyl optionally substituted with one to three halogen atoms,
one C₁-C₄ alkoxy group,
one cyano,
one C₁-C₆ alkylcarbonyloxy group,
one benzylcarbonyloxy group, or
one phenylcarbonyloxy group optionally substituted with one to three halogen atoms
or one C₁-C₄ alkyl group; and

R₇ is phenyl optionally substituted with one or more halogen atoms, C₁-C₄ alkyl groups, C₁-C₄ alkoxy groups, CN groups, NO₂ groups or CF₃ groups.

6. The method according to claim 5 wherein the compound is selected from the group consisting of 4-cyanopyrrole-2-thiocarboxamide; 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-thiocarboxamide; 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N-methyl-5-(trifluoromethyl)pyrrole-3-thiocarboxamide; and 4-(2,3-dichlorophenyl)pyrrole-3-thiocarboxamide.

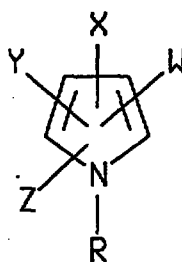
7. The method according to claim 4 further comprising the simultaneous or sequential addition of an insecticidally or acaricidally effective amount of one or more other biological chemicals.

8. A method for protecting growing plants from attack by insects and acarina which comprises





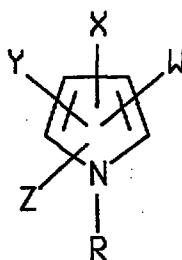
applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally or acaricidally effective amount of a compound having the structural formula



wherein W, X, Y, Z and R are as described in claim 4.

9. The method according to claim 8 wherein the compound is applied to the plants or soil in which they are growing at a rate of about 0.100 kg/ha to 4.0 kg/ha.

10. A composition for controlling insects and acarina comprising an agronomically acceptable carrier and an insecticidally or acaricidally effective amount of a compound having the structural formula



wherein W, X, Y, Z and R are as described in claim 1.



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PYRROLE THIOCARBOXAMIDE INSECTICIDAL AND
ACARICIDAL AGENTS

ABSTRACT OF THE INVENTION

There are provided pyrrole thiocarboxamide compounds which are useful for the control of insects and acarina. Further provided are compositions and methods comprising those compounds for the protection of plants from attack by insects and acarina.

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REPLACED SHEETS		SG
☒	Description : paged 12345 to paged 67890	
☒	Claim(s) : paged 12345 to paged 67890	
☐	Drawing(s) : paged to paged	
☐	Abstract : paged to paged	
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REPLACEMENT SHEETS		SG
☒	Description : paged 12345 to paged 67890	
☒	Claim(s) : paged 12345 to paged 67890	
☐	Drawing(s) : paged to paged	
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PYRROLE THIOCARBOXAMIDE INSECTICIDAL AND

ACARICIDAL AGENTS

10

15

In spite of the commercial insecticides and acaricides available today, damage to crops, both growing and harvested, caused by insects and acarina still occurs. Accordingly, there is ongoing research to create new and more effective insecticides and acaricides.

20

It is therefore an object of the present invention to provide pyrrole thiocarboxamide compounds which are highly effective for controlling insects and acarina.

25

It is also an object of the present invention to provide a method for protecting growing plants from attack by insects and acarina by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally or acaricidally effective amount of a pyrrole thiocarboxamide compound.

These and other objects of the present invention will become more apparent from the detailed description thereof set forth below.

30

The present invention describes pyrrole thiocarboxamide compounds which are highly effective insecticidal and acaricidal agents useful for the control of insect and acarid pests and for protecting agronomic crops from attack by said pests.

35

This invention also relates to insecticidal and acaricidal compositions containing those compounds

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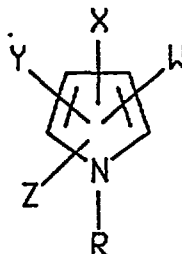
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and methods for using those compounds and compositions for the control of insects and acarina and for the protection of growing or harvested plants from attack by insects and acarina.

5 The insecticidal and acaricidal pyrrole thiocarboxamide compounds of the present invention have the following structural formula I:



10 wherein

15
$$\begin{array}{c} \text{S} \\ || \\ \text{W is } \text{CNR}_1\text{R}_2; \end{array}$$

R_1 and R_2 are each independently hydrogen,

C_1 - C_4 alkyl optionally substituted with one or more halogen atoms, or

20 phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

25 C_1 - C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1 - C_4 alkoxy groups optionally substituted with one or more halogen atoms;

X is Cl, Br, CN, NO_2 , Q,

30 C_1 - C_4 alkyl substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

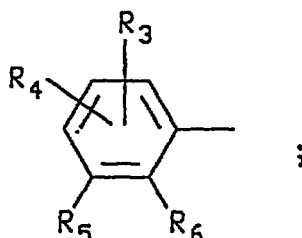
35 CN groups,

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C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or
 C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;

Q is



R_3 and R_4 are each independently hydrogen, halogen,
 NO_2 , CN or C_1-C_4 alkyl optionally substituted with
one or more halogen atoms;

R_5 and R_6 are taken together with the atoms to which
they are attached to form a 5- or 6-membered
heterocyclic ring containing 1 or 2 oxygen atoms
and optionally substituted with one or more
halogen atoms or C_1-C_4 alkyl groups optionally
substituted with one or more halogen atoms;

Y is hydrogen, Cl, Br, CN, NO_2 , $S(O)_nT$, Q,
 C_1-C_4 alkyl substituted with one or more halogen
atoms, or
phenyl optionally substituted with one or more
halogen atoms,

NO_2 groups,
CN groups,
 C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or
 C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;

Z is hydrogen, Cl, Br, $S(O)_nT$ or C_1-C_4 alkyl substi-
tuted with one or more halogen atoms;

T is C_1-C_4 alkyl substituted with one or more halogen
atoms;

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n is an integer of 0, 1 or 2;

R is A, OA or CN;

A is hydrogen, $\overset{\text{O}}{\parallel}\text{CR}_7$, $\text{CHR}_8\overset{\text{O}}{\parallel}\text{NHC}\overset{\text{O}}{\parallel}\text{CR}_9$, CH_2SO_1 ,

- 5 $\text{C}_1\text{-C}_6$ alkyl optionally substituted with one to three halogen atoms,
one tri($\text{C}_1\text{-C}_4$ alkyl)silyl,
one hydroxy,
one cyano,
- 10 one or two $\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one to three halogen atoms,
one $\text{C}_1\text{-C}_4$ alkylthio,
one phenyl optionally substituted with one to three halogen atoms, one to three $\text{C}_1\text{-C}_4$ alkyl groups or one to three $\text{C}_1\text{-C}_4$ alkoxy groups,
- 15 one phenoxy group optionally substituted with one to three halogen atoms, one to three $\text{C}_1\text{-C}_4$ alkyl groups or one to three $\text{C}_1\text{-C}_4$ alkoxy groups,
- 20 one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three $\text{C}_1\text{-C}_4$ alkyl groups or one to three $\text{C}_1\text{-C}_4$ alkoxy groups,
- 25 one $\text{C}_1\text{-C}_6$ alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
- 30 one $\text{C}_2\text{-C}_6$ alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
one phenylcarbonyloxy group optionally sub-

stituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups, one C_1-C_6 alkoxycarbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or

one benzylcarbonyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

C_3-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group, or C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group;

R_7 is C_1-C_6 alkyl or C_3-C_6 cycloalkyl each optionally substituted with one to three halogen atoms, one hydroxy, one cyano, one or two C_1-C_4 alkoxy groups optionally substituted with one to three halogen atoms,

one C_1-C_4 alkylthio, one phenyl group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

one phenoxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl

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- groups or one to three C_1-C_4 alkoxy groups,
- one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
- one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
- one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one C_1-C_6 alkoxy carbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or
- one benzyloxycarbonyl group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- C_2-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group,
- C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group,
- phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, phenoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,
- phenoxy optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, C_1-C_4 alkylthio groups,

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tri(C₁-C₄alkyl)silyl groups, C₁-C₄ alkyl-sulfinyl groups, C₁-C₄ alkylsulfonyl groups, CN groups, NO₂ groups or CF₃ groups,

1- or 2-naphthyl,

2-, 3-, or 4-pyridyl optionally substituted with one to three halogen atoms,

C₁-C₆ alkoxy optionally substituted with one to three halogen atoms, or

C₂-C₆ alkenyloxy optionally substituted with one to three halogen atoms;

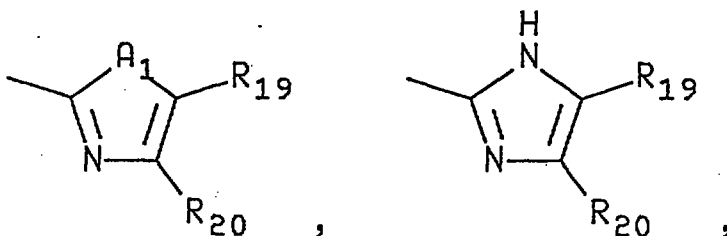
R₈ is hydrogen or C₁-C₄ alkyl;

R₉ is C₁-C₆ alkyl optionally substituted with one to three halogen atoms,

phenyl optionally substituted with one to three halogen atoms, CN groups, NO₂ groups, C₁-C₄ alkyl groups, C₁-C₄ alkoxy groups or CF₃ groups,

2- or 3-thienyl, or
2- or 3-furyl;

Q₁ is $\begin{array}{c} A_1 \\ || \\ C-R_{10} \end{array}$, $\begin{array}{c} A_1 \\ || \\ C-OR_{11} \end{array}$, $\begin{array}{c} A_1 \\ || \\ C-NR_{12}R_{13} \end{array}$, $\begin{array}{c} A_1 \\ || \\ P(OR_{14})_2 \end{array}$, $\begin{array}{c} NR_{15} \\ || \\ C-NR_{16}R_{17} \end{array}$,
 $\begin{array}{c} NR_{15} \\ || \\ C-A_1R_{18} \end{array}$,



CN,

C₁-C₆ alkyl optionally substituted with one or more halogen atoms, CN groups or phenyl groups, or

phenyl optionally substituted with one or more

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halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO_2 groups, CF_3 groups or $NR_{21}R_{22}$ groups;

A_1 is O or S;

5 R_{10} is C_1-C_6 alkyl or phenyl;

R_{11} is C_1-C_6 alkyl;

R_{12} and R_{13} are each independently hydrogen, C_1-C_6 alkyl or may be taken together with the atom to which they are attached to form a 5- to 7-membered ring;

10 R_{14} is C_1-C_4 alkyl;

R_{15} is hydrogen, C_1-C_4 alkyl or may be taken together with either R_{16} or R_{18} and the atoms to which they are attached to form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

15

R_{16} and R_{17} are each independently hydrogen or C_1-C_4 alkyl;

R_{18} is C_1-C_4 alkyl or when taken together with R_{15} and the atoms to which they are attached may form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

20

R_{19} and R_{20} are each independently hydrogen or C_1-C_4 alkyl or when taken together may form a ring wherein $R_{19}R_{20}$ is represented by $-CH=CH-CH=CH-$; and

25

R_{21} and R_{22} are each independently hydrogen or C_1-C_4 alkyl;

with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.

30

Preferred formula I insecticidal and acaricidal pyrrole thiocarboxamide compounds of the invention are those wherein

35
$$W \text{ is } \begin{array}{c} S \\ || \\ CNR_1R_2 \end{array};$$

R_1 and R_2 are each independently hydrogen or C_1-C_4 alkyl;

X is Q or phenyl optionally substituted with one or more halogen atoms,

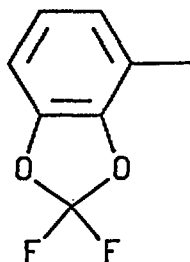
NO₂ groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Q is



Y is hydrogen, Cl, Br, CN, NO₂ or CF₃;

Z is hydrogen, Cl, Br or CF₃;

R is A or CN;

A is hydrogen, $\overset{\text{O}}{\parallel}\text{CR}_7$, or

C_1-C_6 alkyl optionally substituted with one to three halogen atoms,

one C_1-C_4 alkoxy group,

one cyano,

one C_1-C_6 alkylcarbonyloxy group,

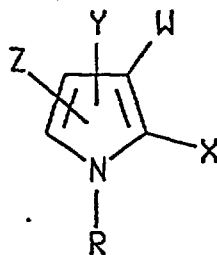
one benzylcarbonyloxy group, or

one phenylcarbonyloxy group optionally substituted with one to three halogen atoms or one C_1-C_4 alkyl group; and

R_7 is phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO₂ groups or CF₃ groups.

More preferred compounds of the present invention are illustrated by formula II and formula III:

5



10

(II)

wherein

15

W is CNR_1R_2 ;

R_1 and R_2 are each independently hydrogen or $\text{C}_1\text{-C}_4$ alkyl;

X is Q or phenyl optionally substituted with one or more halogen atoms,

20

NO_2 groups,

CN groups,

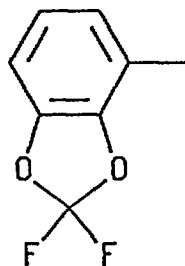
$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or

25

$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;

Q is

30



Y is hydrogen, Cl, Br or CF_3 ;

35

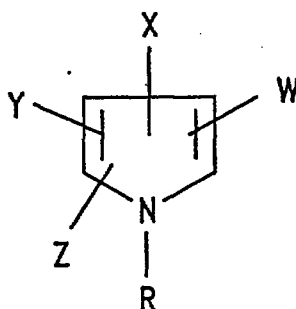
Z is Cl, Br or CF_3 ; and



- 11 -

R is hydrogen or C_1-C_6 alkyl substituted with one C_1-C_4 alkoxy group.

The present invention also relates to novel pyrrole thiocarboxamide compounds having the structural formula



wherein W, X, Y, Z and R are as described hereinabove for formula I with the proviso that when W is on the 3-position of the pyrrole ring and X is on the 4-position of the pyrrole ring and Y, Z and R are each hydrogen, then X is other than 2- or 3-chlorophenyl; and with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H; and with the further proviso that when R_1 and R_2 are both H, then X and Y are other than phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms.

Exemplary of halogen hereinabove are fluorine, chlorine, bromine and iodine.

Advantageously, the present invention provides a method for controlling insects and acarina by contacting said insects and acarina, their breeding

grounds, food supply or habitat with an insecticidally or acaricidally effective amount of a formula I, pyrrole thiocarboxamide compound, provided that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.

The present invention also provides a method for protecting growing plants from attack by insects and acarina by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally or acaricidally effective amount of a formula I, pyrrole thiocarboxamide compound, provided that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.

In practice generally about 10 ppm to 10,000 ppm and preferably 100 ppm to about 5,000 ppm of a formula I pyrrole thiocarboxamide compound, dispersed in water, or another liquid carrier, is effective when applied to the plants, the crops or the soil in which said crops are growing to protect said crops from attack by insects and acarina.

The formula I compounds of this invention are also effective for controlling insects and acarina, when applied to the foliage of plants and/or to the soil or water in which said plants are growing in sufficient amount to provide a rate of from about 0.100 kg/ha to 4.0 kg/ha of active ingredient.

While the compounds of this invention are effective for controlling insects and acarina when employed alone, they may also be used in combination with insecticidally and acaricidally effective amounts of one or more other biological chemicals. For example, the formula I compounds of this invention may be used effectively in conjunction or combination with phosphates, carbamates, cyclodienes, endotoxin of bacillus thuringiensis (Bt), phenol tin compounds,

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pyrethroids, formamidines, chlorinated hydrocarbons, benzoylphenyl ureas and the like.

5 The compounds of the invention may be formulated as emulsifiable concentrates, flowable concentrates, or wettable powders which are diluted with water or other suitable polar solvent, generally in situ, and then applied as a dilute spray. Said compounds may also be formulated in dry compacted granules, granular formulations, dusts, dust concentrates, suspension concentrates, microemulsions and the like
10 all of which lend themselves to seed, soil, water and/or foliage applications to provide the requisite plant protection. Such formulations include the compounds of the invention admixed with inert, solid or liquid diluents.

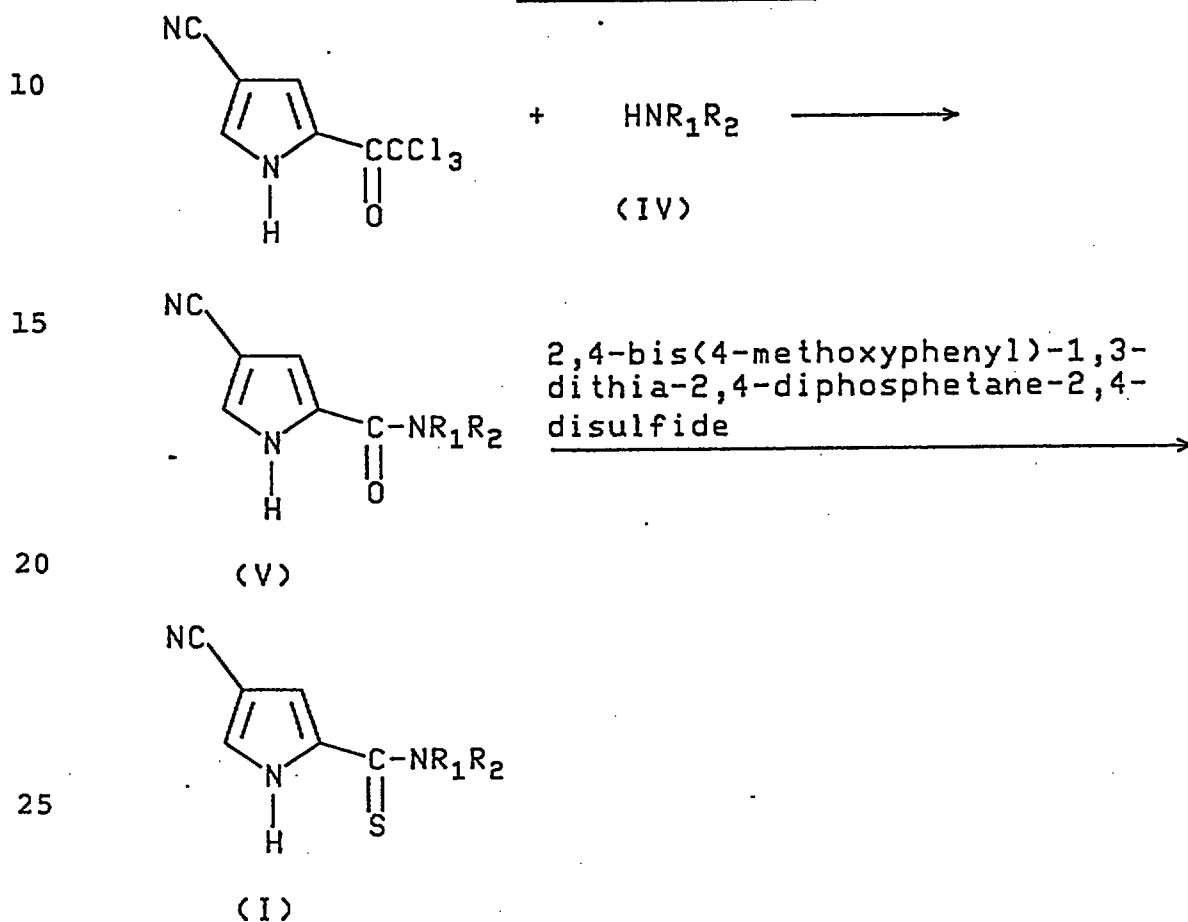
15 For example, wettable powders, dusts, and dust concentrate formulations can be prepared by grinding and blending together about 25% to about 85% by weight of formula I compounds and about 75% to about 15% by weight of a solid diluent such as bentonite,
20 diatomaceous earth, kaolin, attapulgite, or the like, about 1% to about 5% by weight of a dispersing agent such as sodium lignosulfonate, and about 1% to 5% by weight of a nonionic surfactant, such as octylphenoxy polyethoxy ethanol, nonylphenoxy polyethoxy ethanol or
25 the like.

30 A typical emulsifiable concentrate can be prepared by dissolving about 15% to about 70% by weight of a pyrrole thiocarboxamide compound in about 85% to about 30% by weight of a solvent such as isophorone, toluene, butyl cellosolve, methyl acetate, propylene glycol monomethyl ether, or the like and dispersing therein about 1% to 5% by weight of a nonionic surfactant such as an alkylphenoxy polyethoxy alcohol.

Certain formula I compounds of the invention wherein X is CN; Y, Z and R are hydrogen and W is as described above may be prepared as shown in Flow Diagram I.

5

FLOW DIAGRAM I



30

2-Trichloroacetylpyrrole-4-carbonitrile is reacted with at least about one molar equivalent of a formula IV amine compound to give a formula V 4-cyanopyrrole-2-carboxamide compound. The formula V intermediate is then reacted with at least about one molar

35

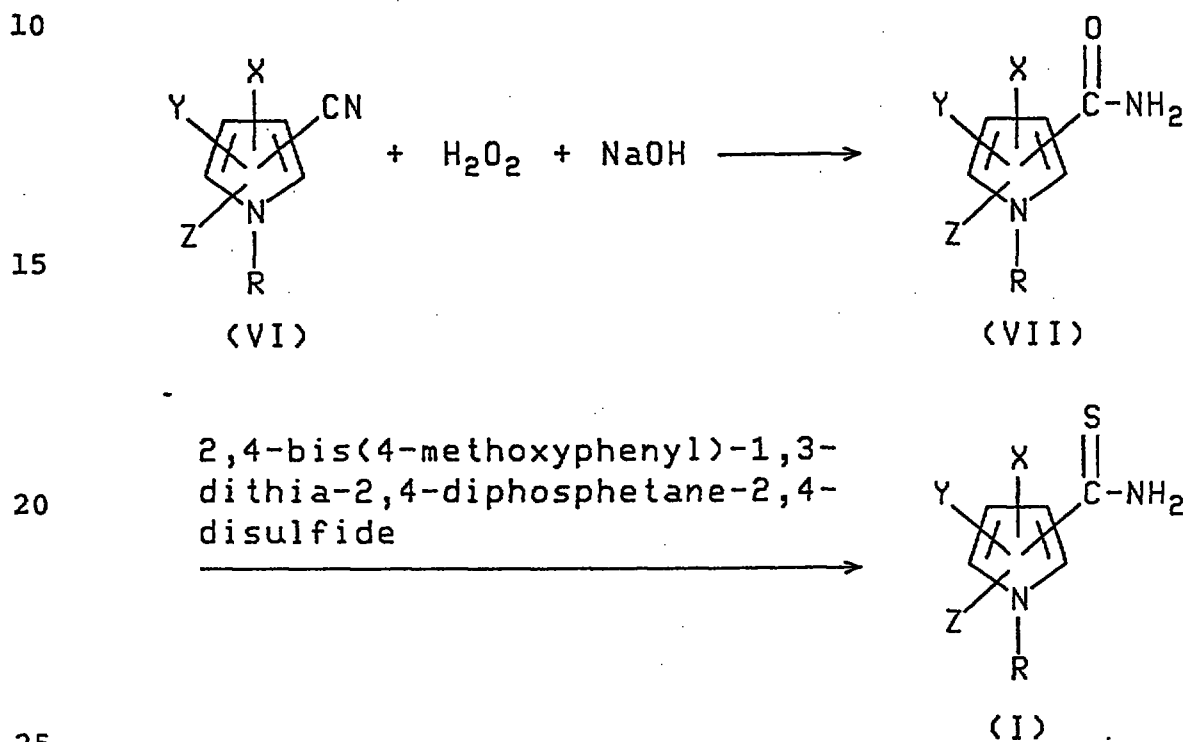
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equivalent of a reagent capable of introducing the thioxo group, such as 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, to give the desired 4-cyanopyrrole-2-thiocarboxamide of formula I.

Other insecticidal and acaricidal compounds of formula I may be prepared as shown in Flow Diagram II.

FLOW DIAGRAM II

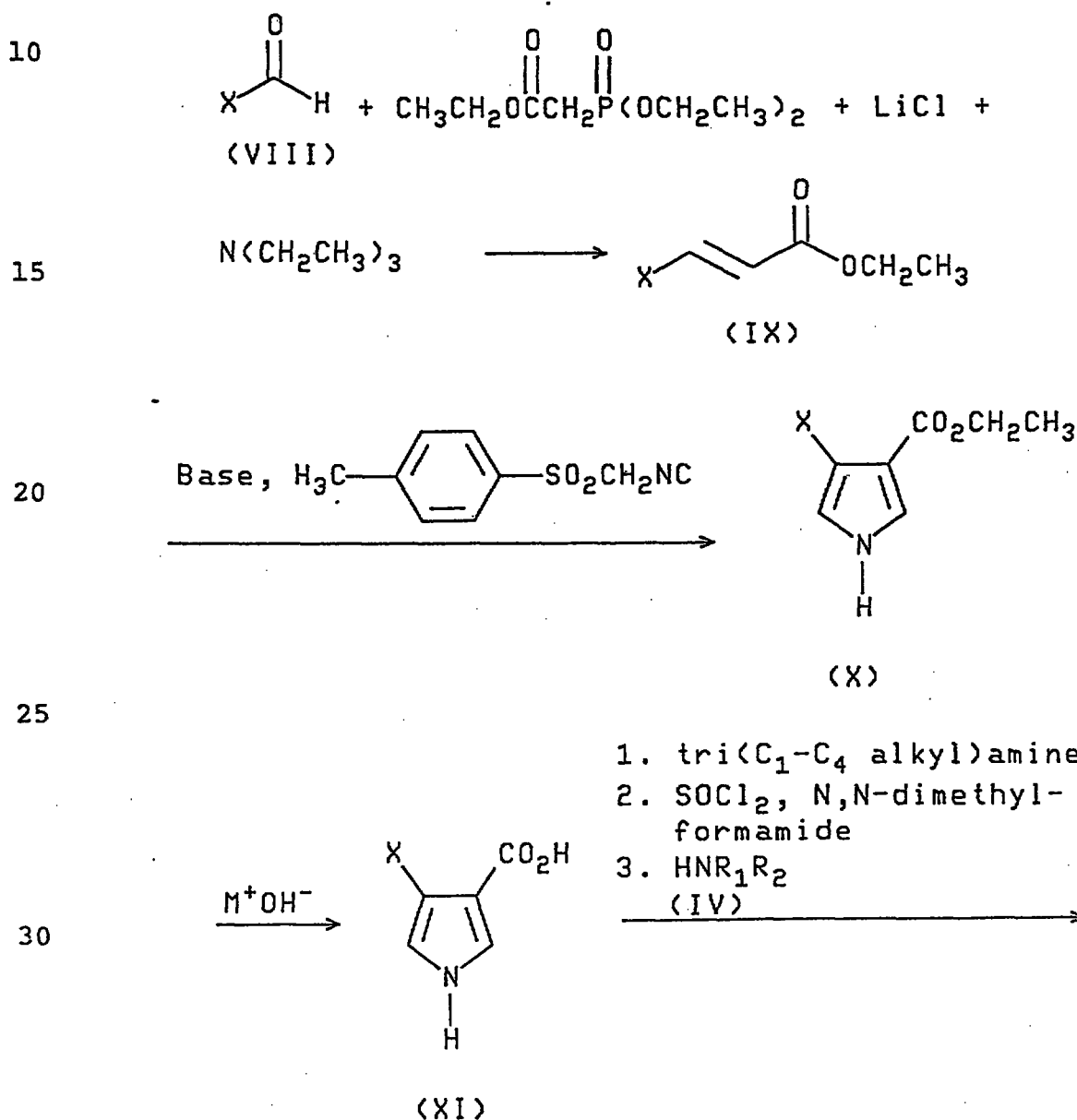


The appropriately substituted formula VI cyanopyrrole is reacted with an excess of hydrogen peroxide and sodium hydroxide to give the appropriately substituted formula VII pyrrole carboxamide. The intermediate formula VII compound is then reacted with at least about one molar equivalent of a reagent capable of introducing the thioxo group, such as 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-

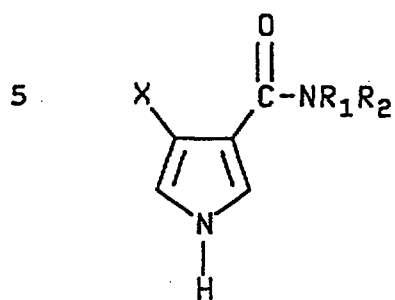
2,4-disulfide, to give the appropriately substituted formula I pyrrole thiocarboxamide compound.

Certain insecticidal and acaricidal 4-(substituted phenyl)pyrrole-3-thiocarboxamide compounds of formula I may be prepared as shown in Flow Diagram III.

FLOW DIAGRAM III

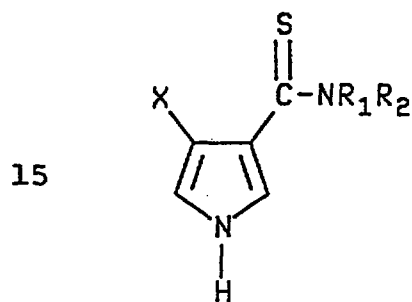


FLOW DIAGRAM III (Continued)



(XII)

2,4-bis(4-methoxyphenyl)-1,3-dithia-
2,4-diphosphetane-2,4-disulfide



(I)

wherein

X is Q or phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

25 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

30 M is an alkali metal; and

Q, R₁ and R₂ are as described hereinabove for formula I.

35 The appropriately substituted formula VIII benzaldehyde is reacted with at least about one molar equivalent each of triethyl phosphonoacetate, lithium

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chloride and triethylamine to give the appropriately substituted ethyl cinnamate of formula IX. The formula IX cinnamate is reacted with at least about one molar equivalent of a strong base such as sodium hydride and at least about one molar equivalent of tosylmethyl isocyanide to give a formula X ethyl 4-(substituted phenyl)pyrrole-3-carboxylate which is hydrolyzed with an alkali metal hydroxide such as potassium hydroxide to give a formula XI 4-(substituted phenyl)pyrrole-3-carboxylic acid. The formula XI carboxylic acid is reacted with an excess of a tri(C₁-C₄ alkyl)amine to form a first mixture. The first mixture is reacted with an excess of thionyl chloride and at least about one molar equivalent of N,N-dimethylformamide to give a second mixture. The second mixture is reacted with an excess of a formula IV amine compound to give the formula XII 4-(substituted phenyl)pyrrole-3-carboxamide and reacting the formula XII carboxamide with a reagent capable of introducing the thioxo group, such as 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, to give the desired insecticidal and acaricidal 4-(substituted phenyl)pyrrole-3-thiocarboxamide of formula I.

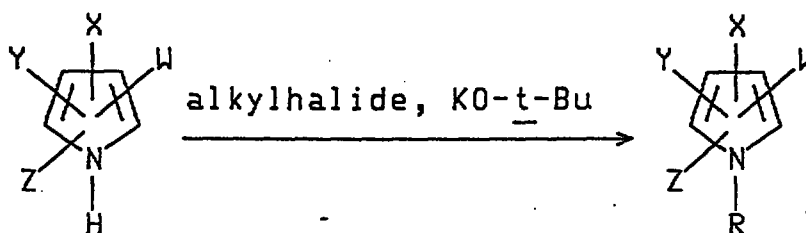
Preparation of 1-substituted formula I pyrrole thiocarboxamide compounds can be achieved by reaction of the appropriately substituted formula I pyrrole thiocarboxamide having R as hydrogen with an alkylating or acylating agent in the presence of an alkali metal alkoxide or hydride. For example, a formula I pyrrole thiocarboxamide, wherein R is hydrogen and W, X, Y and Z are as described for formula I above, is reacted with an appropriate alkylating agent such as a C₁-C₆ alkylhalide in which the alkyl group is straight or branched and is optionally substituted with from one to three halogen atoms, one hydroxy, one

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cyano, one C_1-C_4 alkoxy, one C_1-C_4 alkylthio, one phenyl group optionally substituted with from one to three halogen atoms, or one benzyloxy group optionally substituted with from one to three halogen atoms, and an alkali metal alkoxide such as sodium or potassium *t*-butoxide. This reaction provides a pyrrole thiocarboxamide having the same substituents as the starting material, but in addition is substituted on the nitrogen with a C_1-C_6 alkyl group optionally substituted as described above. This reaction may be illustrated as follows:



wherein W, X, Y and Z are as described for formula I above and R is C_1-C_6 alkyl optionally substituted as described above. In a similar reaction cyanogen bromide is substituted for the alkylhalide and yields the formula I pyrrole thiocarboxamide having a carbonitrile, rather than an alkyl group on the 1-position.

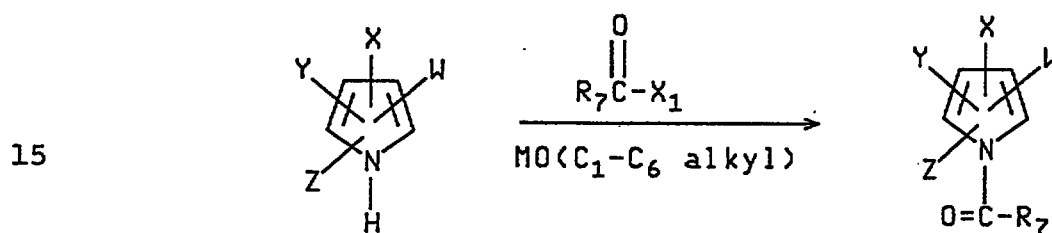
Advantageously, the above-described alkylation procedure of the formula I pyrrole thiocarboxamide compounds in which R is hydrogen may also be applied to the preparation of formula I pyrrole thiocarboxamides having an $N-C_3-C_6$ alkenyl or $N-C_3-C_6$ alkynyl substituent. This substitution is obtained by simply substituting a C_3-C_6 alkenyl halide or C_3-C_6 alkynyl halide for the C_1-C_6 alkyl halide in the above-described reaction.

In a similar manner, preparation of 1-acylated pyrrole thiocarboxamides may be achieved by the reaction of an appropriately substituted formula I

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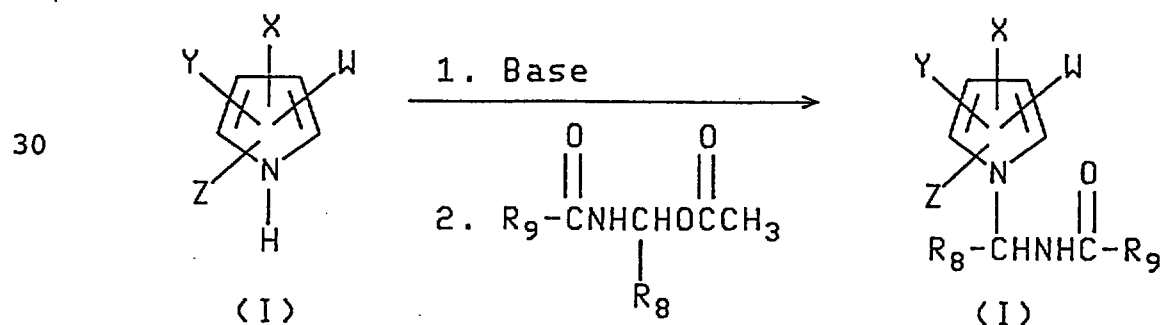
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pyrrole thiocarboxamide wherein R is hydrogen with an acylating agent in the presence of an alkali metal alkoxide. Acylating agents such as C₁-C₆ alkyl or C₂-C₆ alkenyl acid chlorides, substituted C₁-C₆ alkyl or C₂-C₆ alkenyl acid chlorides, benzoyl chloride, substituted benzoyl chlorides, phenylchloroformate, substituted phenylchloroformates, C₁-C₆ alkyl or C₂-C₆ alkenylchloroformates, substituted C₁-C₆ alkyl or C₂-C₆ alkenylchloroformates, N-substituted carbamoyl chlorides and the like may be employed. The reaction may be illustrated as follows:



wherein X₁ is halogen, M is an alkali metal and W, X, Y, Z and R₇ are as described hereinabove for formula I.

20 Formula I pyrrole thiocarboxamide compounds wherein R is CH₂SO₁ may be prepared by reaction of the appropriately substituted formula I pyrrole thiocarboxamide having A as chloromethyl with an alkali metal salt of an SO₁ compound in the presence of a base. And
25 formula I pyrrole thiocarboxamide compounds wherein R is CHR₈NHC(O)R₉ may be prepared as shown below.

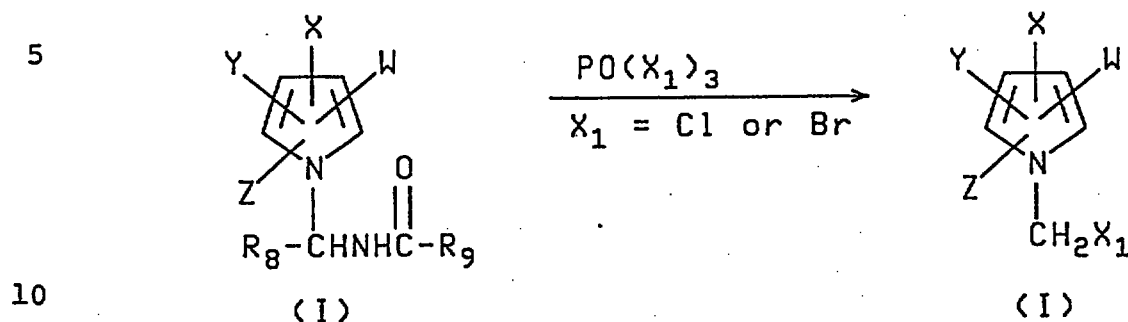


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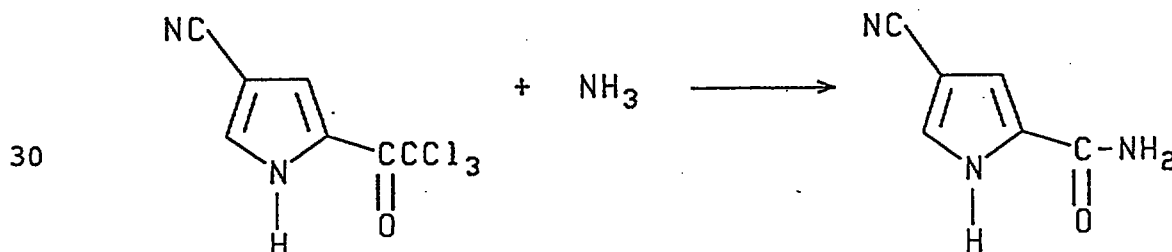
Advantageously, 1-halomethyl pyrrole thio-carboxamides of formula I may be prepared as shown below.



In order to facilitate a further understanding of the invention, the following examples are presented primarily for the purpose of illustrating more specific details thereof. The examples generally utilize the above reaction schemes and also provide further means for preparing even more compounds of the present invention which are not specifically described above. The invention should not be deemed limited by the examples as the full scope of the invention is defined in the claims.

EXAMPLE 1

Preparation of 4-Cyanopyrrole-2-carboxamide



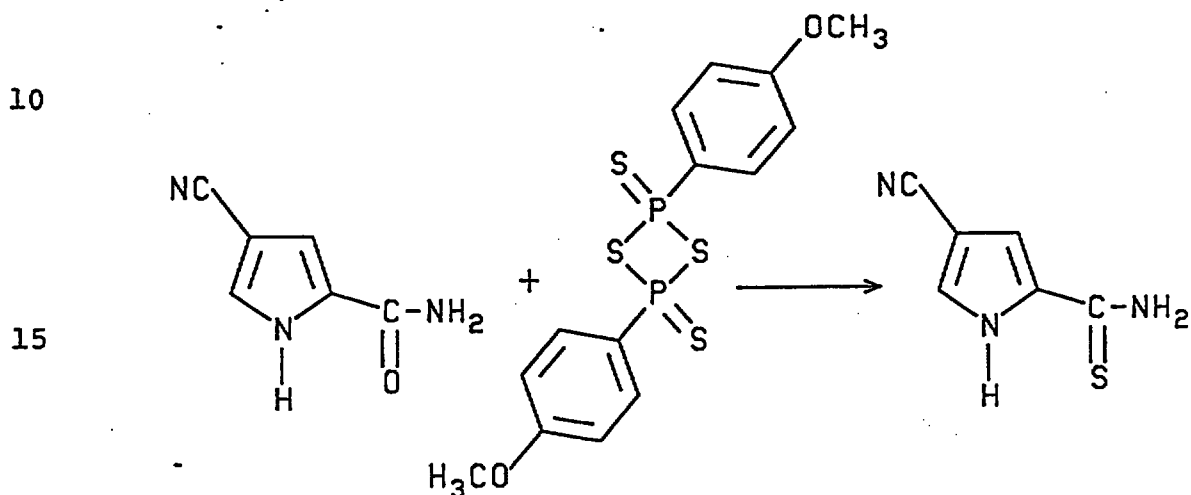
A solution of 2-trichloroacetylpyrrole-4-carbonitrile (20 g, 84.2 mmol) in methanol is treated

with ammonia (51 mL), stirred at room temperature for 30 minutes and diluted with water. The aqueous mixture is filtered to obtain the title product as a white solid (7.0 g, mp 253^o-256^oC).

5

EXAMPLE 2

Preparation of 4-Cyanopyrrole-2-thiocarboxamide



20 A mixture of 4-cyanopyrrole-2-carboxamide (1.35 g, 10.0 mmol) and 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (4.0 g, 9.9 mmol) in toluene is heated at 100^oC for 4 1/2 hours, diluted with tetrahydrofuran and heated at reflux for

25 20 minutes. The reaction mixture is then cooled and concentrated in vacuo to obtain a residue. Chromatography of the residue using silica gel and a 4:1 hexanes/ethyl acetate mixture gives the title product as a yellow solid (0.9 g, mp 253^oC dec.).

30

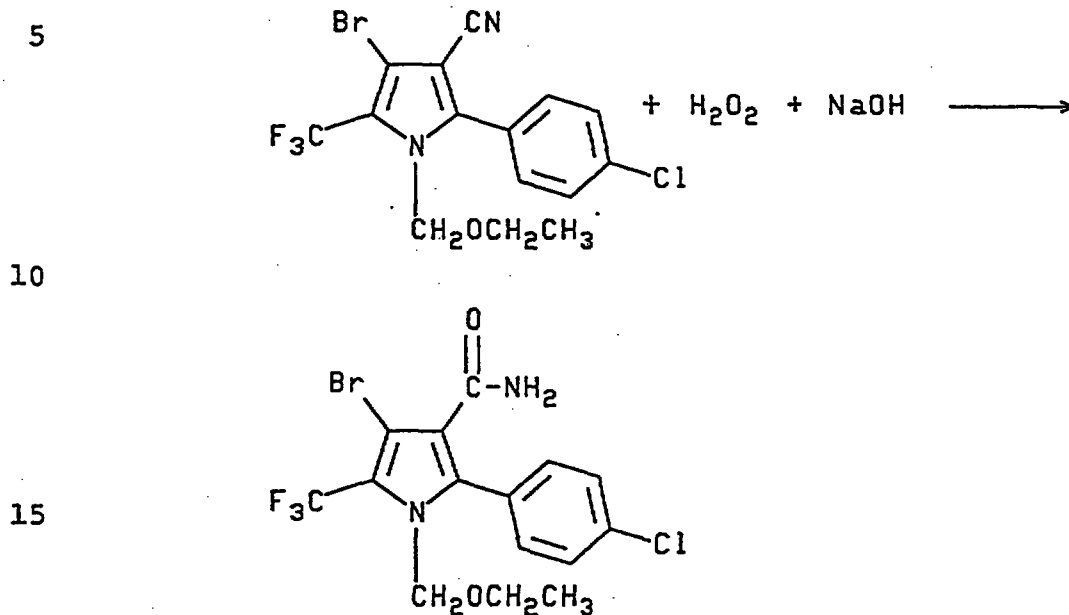
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EXAMPLE 3

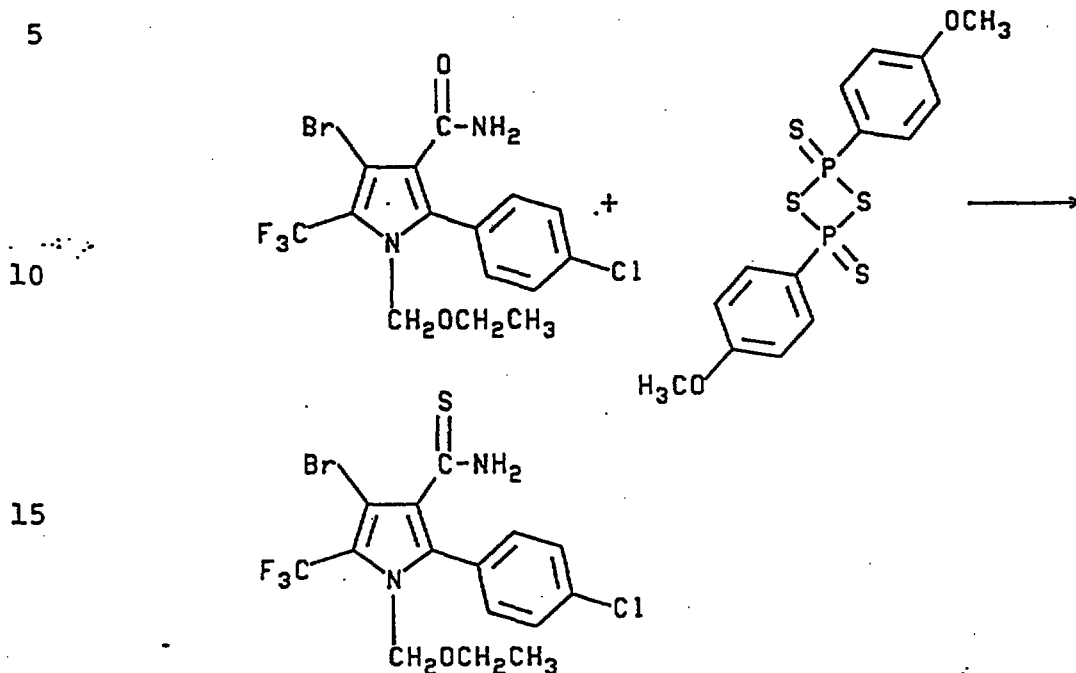
Preparation of 4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxamide



A mixture of 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carbo-
20 nitrile (4.07 g, 10 mmol), sodium hydroxide (0.8 g, 20 mmol) and 30 wt/wt% hydrogen peroxide solution (7.2 mL, 70 mmol) in methanol is stirred at room temperature for 7 hours, treated with sodium hydroxide solution (0.8 g NaOH in 5 mL of H₂O) and 30 wt/wt% hydrogen peroxide
25 solution (7 mL), stirred at room temperature overnight, heated at 40°C for 8 hours and diluted with water. The aqueous mixture is filtered and the filter cake is washed with water and heptane and dried to give the title product as a white solid (3.7 g) which is identi-
30 fied by ¹H and ¹³C NMR spectral analyses.

EXAMPLE 4

Preparation of 4-Bromo-2-(p-chlorophenyl)-1-ethoxymethyl-5-(trifluoromethyl)pyrrole-3-thiocarboxamide



20 A mixture of 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxamide (3.9 g, 9.2 mmol) and 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (5.7 g, 14.1 mmol) in acetonitrile is heated at reflux for 6 hours, cooled and concentrated in vacuo to obtain a residue.

25 Chromatography of the residue using silica gel and a 4:1 hexanes/ethyl acetate mixture gives the title product as a yellow solid (1.5 g, mp 163°-172°C).

30

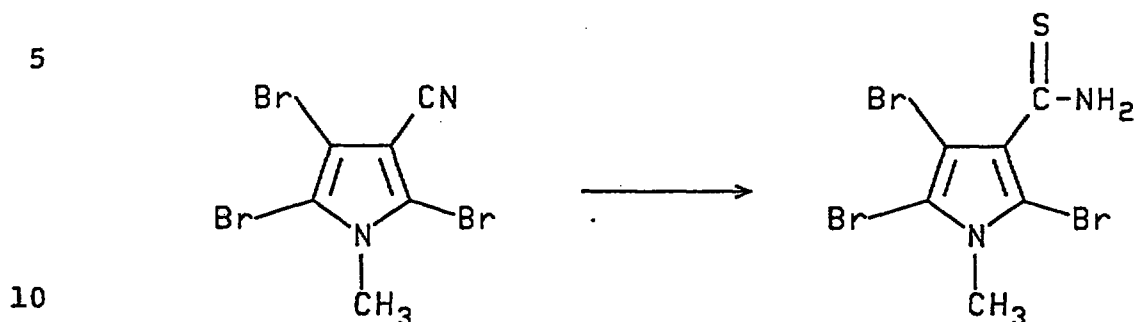
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EXAMPLE 5

Preparation of 2,4,5-Tribromo-1-methylpyrrole-3-thio-carboxamide



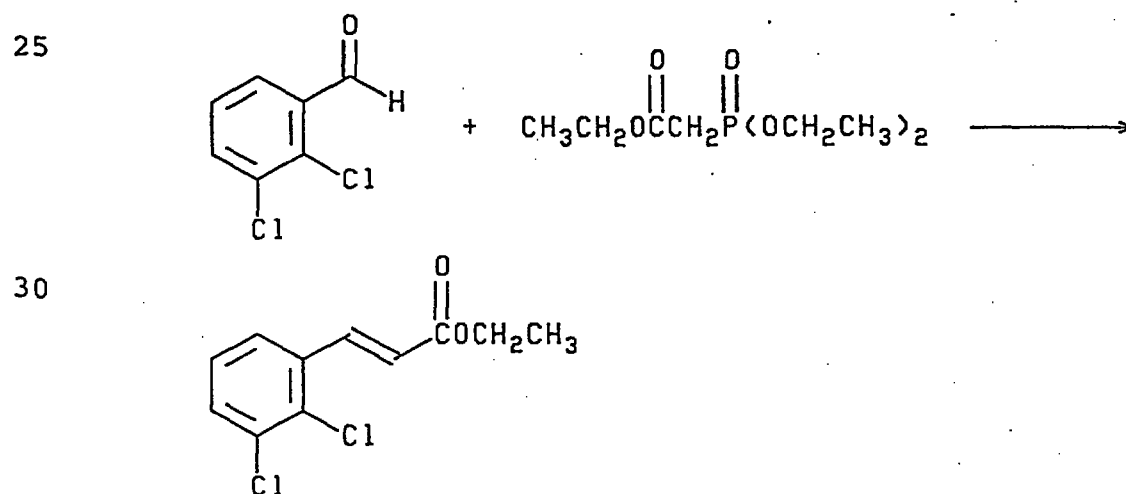
Diisopropylethylamine (1.1 mL, 6 mmol), 2,4,5-tribromo-1-methylpyrrole-3-carbonitrile (2.16 g, 6 mmol) and pyridine (10 mL) are added to condensed hydrogen sulfide in a pressure tube at -78°C . The tube is sealed and the reaction mixture is stirred for 5 days at room temperature. The reaction mixture is then concentrated in vacuo to obtain a residue. Chromatography of the residue using silica gel and a 4:1 hexanes/ethyl acetate mixture gives the title product as a yellow solid (0.47 g, mp 100.5°C - 102°C dec.).

15

20

EXAMPLE 6

Preparation of Ethyl 2,3-dichlorocinnamate, (E)-



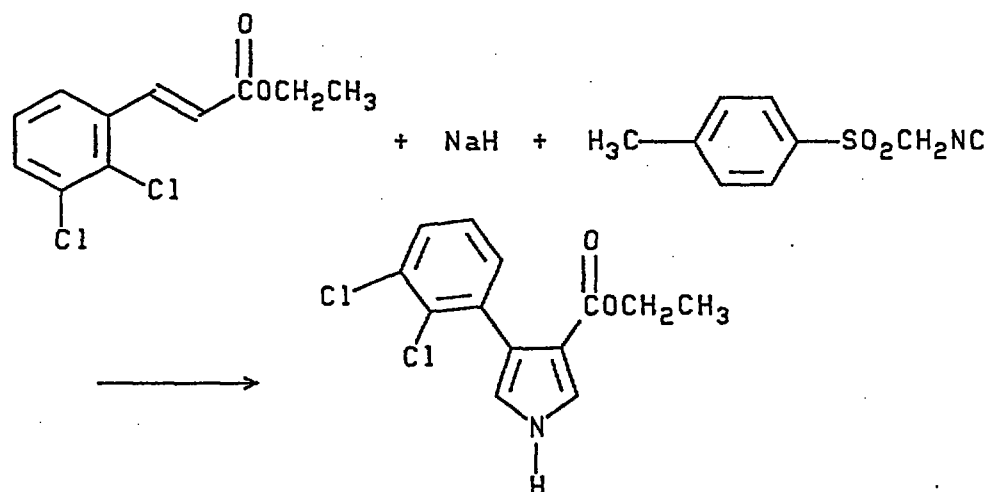
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A mixture of 2,3-dichlorobenzaldehyde (17.5 g, 0.1 mol), triethyl phosphonoacetate (22.4 g, 0.12 mol), lithium chloride (5.1 g, 0.12 mol) and triethylamine (17 mL, 0.12 mol) in acetonitrile is stirred at room temperature for 1 hour and diluted with a water/ethyl acetate mixture. The organic phase is separated, washed with water dried over anhydrous Na_2SO_4 and concentrated in vacuo to give the title product as a yellow solid (42 g).

EXAMPLE 7

Preparation of Ethyl 4-(2,3-dichlorophenyl)pyrrole-3-carboxylate



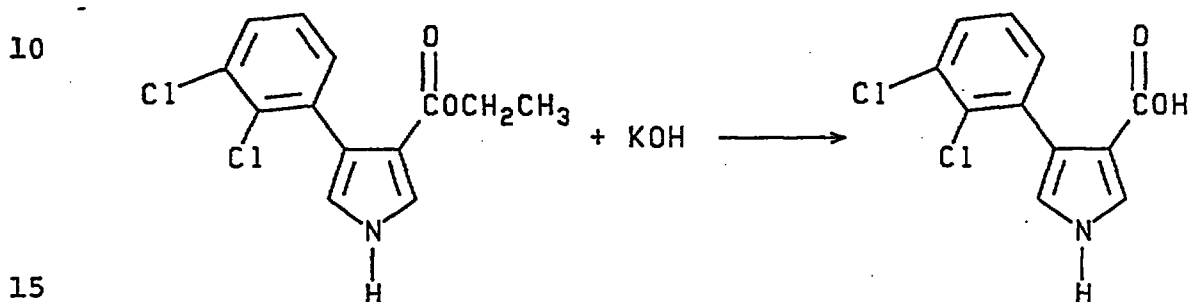
Sodium hydride (3.2 g, 60% in mineral oil) is washed with petroleum ether and suspended in tetrahydrofuran. A mixture of ethyl 2,3-dichlorocinnamate, (E)- (12.25 g, 50 mmol) and tosylmethyl isocyanide (11.7 g, 60 mmol) in tetrahydrofuran is added to the sodium hydride/tetrahydrofuran mixture. The reaction mixture is stirred for 1 hour, quenched with saturated ammonium chloride solution and extracted with diethyl ether. The organic extracts are combined, washed with water, dried over anhydrous Na_2SO_4 and concentrated in vacuo to obtain a residue. Chromatography of the

residue using silica gel and a 2:1 hexanes/ethyl acetate mixture gives the title product as a white solid (6.5 g) which is identified by ^1H and ^{13}C NMR spectral analyses.

5

EXAMPLE 8

Preparation of 4-(2,3-Dichlorophenyl)pyrrole-3-carboxylic acid



15

A mixture of ethyl 4-(2,3-dichlorophenyl)pyrrole-3-carboxylate (5.95 g, 21 mmol) and potassium hydroxide (6.5 g, 85%, 99 mmol) is heated at reflux for

20

6 hours, cooled, diluted with water and washed with diethyl ether. The aqueous phase is acidified with hydrochloric acid and filtered to obtain a solid. The solid is washed with diethyl ether and petroleum ether and dried to give the title product as a white solid

25

(5.24 g) which is identified by ^1H and ^{13}C NMR spectral analyses.

30

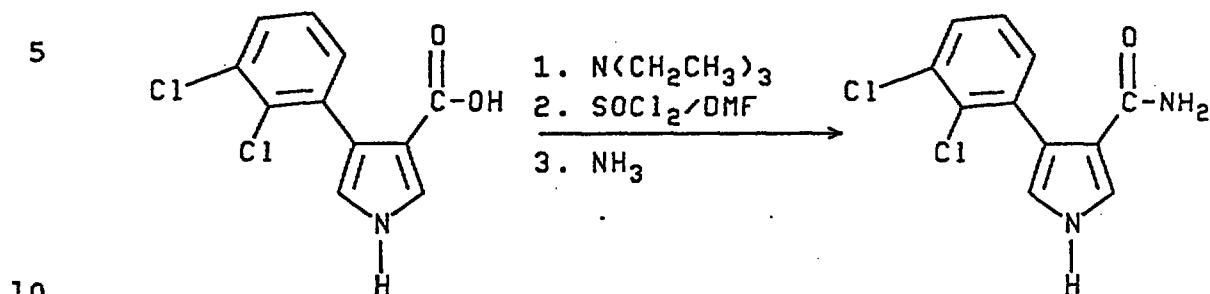
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EXAMPLE 9

Preparation of 4-(2,3-Dichlorophenyl)pyrrole-3-carbo-
xamide



15 A mixture of 4-(2,3-dichlorophenyl)pyrrole-3-carboxylic acid (2.43 g, 9.5 mmol) and triethylamine (7 mL, 50 mmol) in tetrahydrofuran is stirred for 15 minutes at room temperature and concentrated in vacuo to obtain a residue. A mixture of the residue, thionyl chloride (2.77 mL, 38 mmol) and N,N-dimethylformamide (0.73 mL, 9.5 mmol) is stirred overnight at room temperature and concentrated in vacuo to obtain a yellow oil. The oil is added to a concentrated ammonia solution and stirred for 1 hour. This mixture is filtered to give a solid. The solid is washed with water, dried and chromatographed using silica gel and a 4:1 hexanes/ethyl acetate mixture to obtain the title product as a white solid (1.6 g, mp $185^\circ\text{--}190^\circ\text{C}$).

25 Using essentially the same procedure, but substituting the appropriate amine for ammonia, the following compounds are obtained:

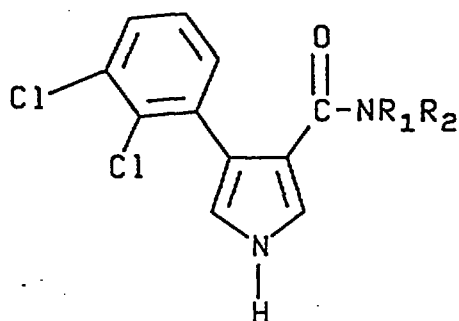
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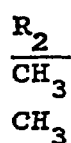
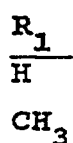
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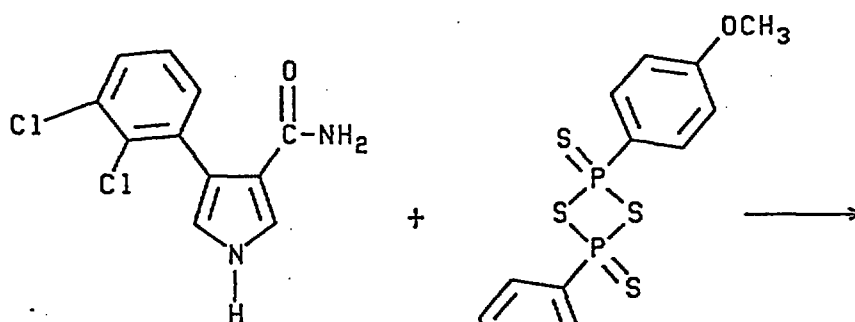
mp °C
134 - 137
133 - 136

EXAMPLE 10

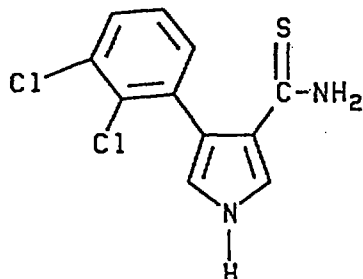
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Preparation of 4-(2,3-Dichlorophenyl)pyrrole-3-thio-
carboxamide

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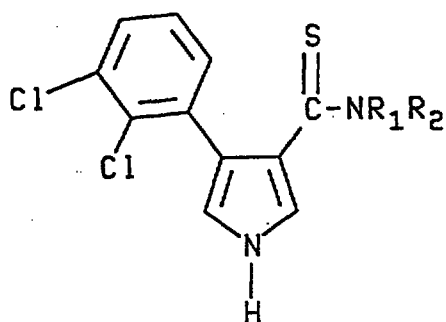
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A mixture of 4-(2,3-dichlorophenyl)pyrrole-3-carboxamide (0.98 g, 3.8 mmol) and 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (0.77 g, 1.9 mmol) in tetrahydrofuran is heated at

35

reflux for 75 minutes, cooled and concentrated in vacuo to obtain a residue. Chromatography of the residue using silica gel and a 1:1 hexane/ethyl acetate mixture gives the title product as a yellow solid (0.54 g, mp 128°-132°C).

5. Using essentially the same procedure, but using the appropriately substituted pyrrole carboxylic amide, the following compounds are obtained:



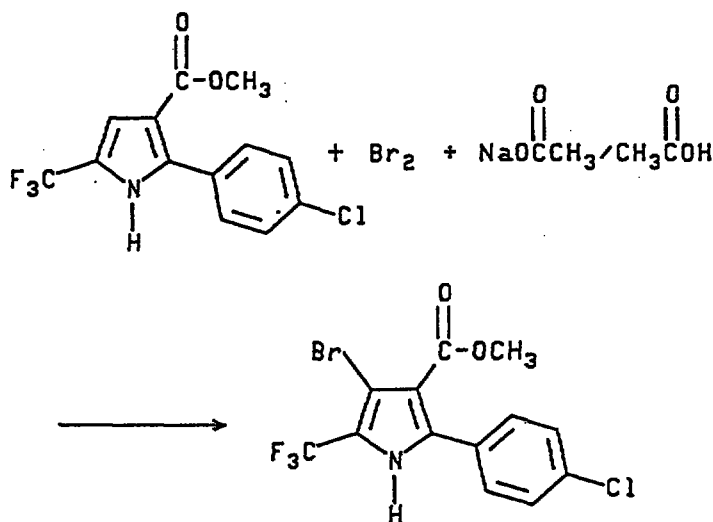
$\frac{R_1}{H}$
 $\frac{R_1}{CH_3}$

$\frac{R_2}{CH_3}$
 $\frac{R_2}{CH_3}$

$\frac{mp^\circ C}{158 - 162}$
 $\frac{mp^\circ C}{226 - 229}$

EXAMPLE 11

Preparation of Methyl 4-bromo-2-(p-chlorophenyl)-5-(trifluoromethyl)pyrrole-3-carboxylate



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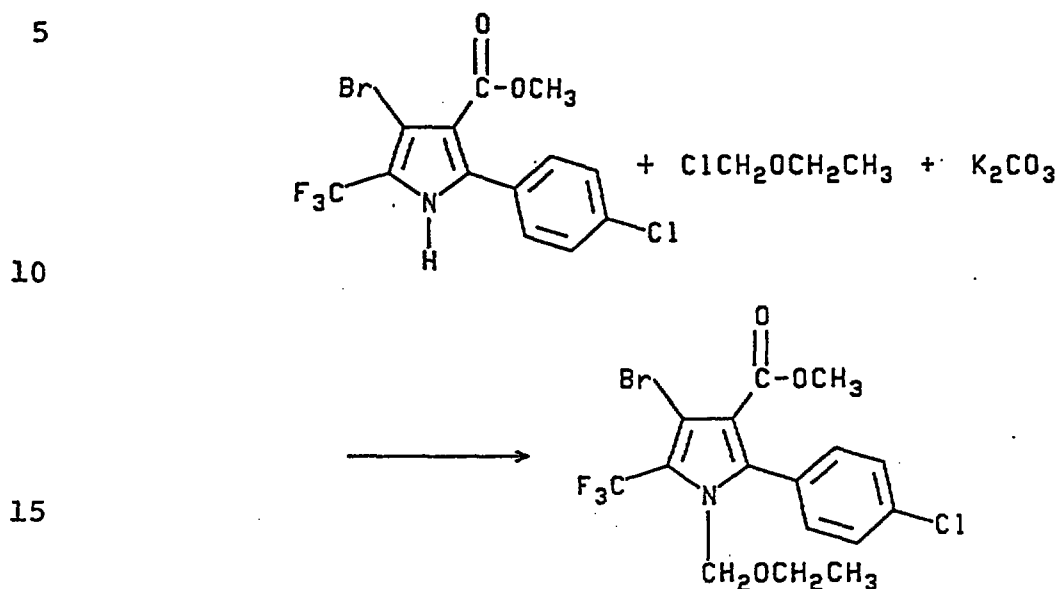
Bromine (2.3 mL, 43.7 mmol) is added to a solution of methyl 2-(p-chlorophenyl)-5-(trifluoromethyl)pyrrole-3-carboxylate (8.44 g, 29.2 mmol) and sodium acetate (3.6 g, 43.7 mmol) in acetic acid. The reaction mixture is stirred for 30 minutes, diluted with a 0.4 wt/wt% sodium sulfite solution and extracted with diethyl ether. The organic extracts are combined, washed with saturated sodium hydrogen carbonate solution, dried over anhydrous Na₂SO₄ and concentrated in vacuo to obtain an oil which solidifies to give the title product as a solid (9.2 g) which is identified by ¹H and ¹³C NMR spectral analyses.

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EXAMPLE 12

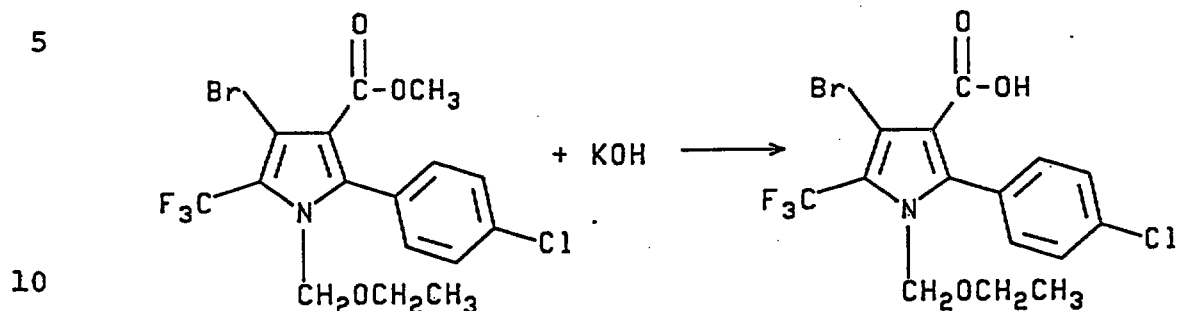
Preparation of Methyl 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxylate



20 A mixture of methyl 4-bromo-2-(p-chloro-phenyl)-5-(trifluoromethyl)pyrrole-3-carboxylate (9.2 g, 24.1 mmol), potassium carbonate (4.96 g, 36 mmol) and chloromethyl ethyl ether (3.3 mL, 36 mmol) is stirred at room temperature for 21 hours, treated with potassium carbonate (4.9 g) and chloromethyl ethyl ether (3.3 mL), stirred for 1 hour, treated with potassium carbonate (4.9 g) and chloromethyl ethyl ether (3.3 mL) stirred for 3 hours, diluted with water and extracted with diethyl ether. The combined organic extracts are washed with water, dried over anhydrous MgSO_4 and concentrated in vacuo to obtain the title product as a brown oil (13.1 g) which is used in the next step without further purification.

EXAMPLE 13

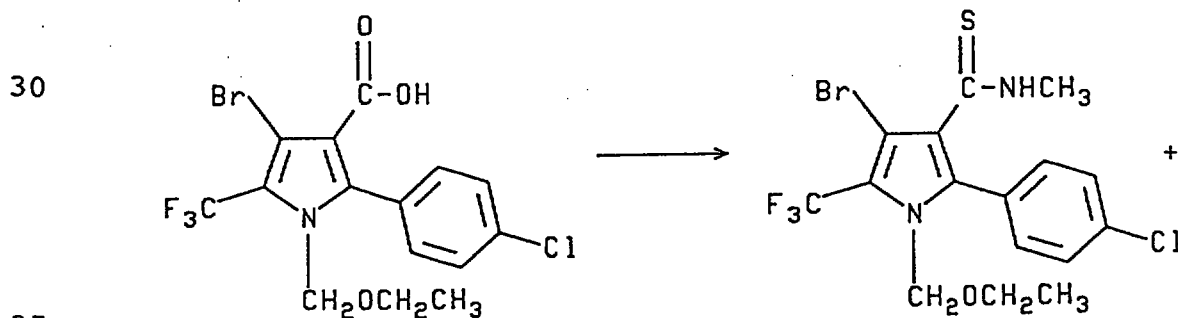
Preparation of 4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxylic acid



A mixture of methyl 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxylate (13.1 g) and potassium hydroxide (3.12 g, 85%, 48 mmol) is stirred at room temperature for 20 hours, stirred at reflux for 2 hours, diluted with water, washed with diethyl ether, acidified to pH 4 with 1N hydrochloric acid and filtered to obtain a solid. The solid is washed with water and petroleum ether and dried to give the title product as a white solid (6.45 g) which is identified by ¹H NMR spectral analysis.

EXAMPLE 14

25 **Preparation of 4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N-methyl-5-(trifluoromethyl)pyrrole-3-thio-carboxamide**



Isobutylchloroformate (0.3 mL, 2.3 mmol) is added to a mixture of 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carboxylic acid (0.83 g, 2 mmol) and triethylamine (0.33 mL, 2.3 mmol) in tetrahydrofuran at 0°C. The mixture is stirred for 1 hour at 0°C, treated with a 6 wt/wt% methylamine solution (10.6 g, 20 mmol), stirred at room temperature for 2 hours and diluted with a diethyl ether/water mixture. The organic phase is separated, dried over anhydrous Na₂SO₄, concentrated in vacuo, diluted with toluene and concentrated in vacuo to obtain a liquid. A mixture of the liquid in tetrahydrofuran is treated with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (0.40 g, 1 mmol), heated at reflux for 2 hours, concentrated in vacuo and chromatographed on silica gel with a 4:1 hexane/ethyl acetate mixture to obtain the title product as a yellow gum (0.3 g) which is identified by ¹H and ¹³C NMR spectral analyses.

Using essentially the same procedure, but substituting dimethylamine for methylamine, 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N,N-dimethyl-5-(trifluoromethyl)pyrrole-3-thiocarboxamide is obtained as a yellow gum.

EXAMPLE 15

Insecticide and acaricide evaluations

The following tests show the efficacy of the compounds as insecticides and acaricides. The evaluations are conducted with solutions of test compounds dissolved or dispersed in 50/50 acetone/water mixtures. The test compound is technical material dissolved or dispersed in said acetone/water mixtures in sufficient amount to provide the concentrations set forth in Table I below.

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All concentrations reported herein are in terms of active ingredient. All tests are conducted in a laboratory maintained at about 27°C. The rating system employed is as follows:

5

Rating System

	0 = no effect	5 = 56-65% kill
	1 = 10-25% kill	6 = 66-75% kill
10	2 = 26-35% kill	7 = 76-85% kill
	3 = 36-45% kill	8 = 86-99% kill
	4 = 46-55% kill	9 = 100% kill
		- = not evaluated

15 The test species of insects used in the present evaluations along with specific test procedures are described below.

Spodoptera eridania 3rd instar larvae, southern army-worm

20 A sieva lima bean leaf expanded to 7 to 8 cm in length is dipped in the test suspension with agitation for 3 seconds and placed in a hood to dry. The leaf is then placed in a 100x10 mm petri dish containing a damp filter paper on the bottom and 10 3rd instar caterpillars. The dish is maintained for 5 days before
25 observations are made of mortality, reduced feeding, or any interference with normal moulting.

Tetranychus urticae (OP-resistant strain), 2-spotted spider mite

30 Sieva lima bean plants with primary leaves expanded to 7 to 8 cm are selected and cut back to one plant per pot. A small piece is cut from a leaf taken from the main colony and placed on each leaf of the
35 test plants. This is done about 2 hours before

treatment to allow the mites to move over to the test plant and to lay eggs. The size of the cut piece is varied to obtain about 100 mites per leaf. At the time of the treatment, the piece of leaf used to transfer the mites is removed and discarded. The mite-infested plants are dipped in the test formulation for 3 seconds with agitation and set in the hood to dry. Plants are kept for 2 days before estimates of adult kill are made.

10

Heliothis virescens, 3rd instar tobacco budworm

Cotton cotyledons are dipped in the test formulation and allowed to dry in a hood. When dry, each is cut into quarters and ten sections placed individually in 30 mL plastic medicine cups containing a 5 to 7 mm long piece of damp dental wick. One 3rd instar caterpillar is added to each cup and a cardboard lid is placed on the cup. Treatments are maintained for 3 days before mortality counts and estimates of reduction in feeding damage are made.

20

Dibrotica undecimpunctata howardi, 3rd instar southern corn rootworm

One cc of fine talc is placed in a 30 mL wide-mouth screw-top glass jar. One mL of the appropriate acetone test solution is pipetted onto the talc so as to provide 1.25 mg and 0.25 mg of active ingredient per jar. The jars are set under a gentle air flow until the acetone is evaporated. The dried talc is loosened, 1 cc of millet seed is added to serve as food for the insects and 25 mL of moist soil is added to each jar. The jars are capped and contents thoroughly mixed on a Vortex Mixer. Following this, ten 3rd instar rootworms are added to each jar and the jars are loosely capped to allow air exchange for the

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larvae. The treatments are held for 6 days before mortality counts are made. Missing larvae are presumed dead, since they decompose rapidly and can not be found. The concentrations used in this test correspond
5 approximately to 50 kg/ha and 10 kg/ha, respectively.

The data obtained for the above described evaluations are reported in Table I.

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TABLE I

Insecticide and Acaricide Evaluations

Compound	OP.					
	Resistant		Tobacco		Southern Corn	
	Armyworm	Mites	Budworm	Budworm	Rootworm	Rootworm
	(ppm)	(ppm)	(ppm)	(ppm)	(kg/ha)	(kg/ha)
	1000	300	100	100	50	10
4-Cyanopyrrole-2-thiocarbonyl xamide	9	0	-	-	9	-
4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-thiocarbonyl xamide	9	9	9	9	9	9
4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N-methyl-5-(trifluoromethyl)pyrrole-3-thiocarbonyl xamide	-	3	-	8	-	-

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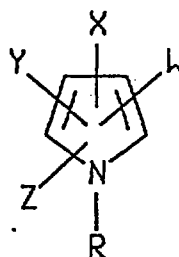
TABLE I (Continued)

Compound	OP.				
	Armyworm		Resistant		Tobacco
	(ppm)		Mites	Budworm	Southern Corn
	1000	100	10	300	100
				(ppm)	(kg/ha)
					Rootworm

4-Bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N,N-dimethyl-5-(trifluoromethyl)pyrrole-3-thiocarboxamide

I CLAIM:

1. A compound having the structural formula



wherein

W is $\text{C}(\text{S})\text{NR}_1\text{R}_2$;

R_1 and R_2 are each independently hydrogen,

$\text{C}_1\text{-C}_4$ alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or

$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;

X is Cl, Br, CN, NO_2 , Q,

$\text{C}_1\text{-C}_4$ alkyl substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or

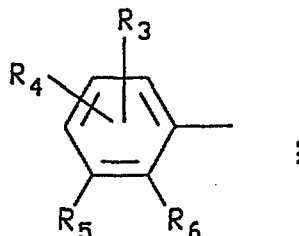
$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;



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Q is



R_3 and R_4 are each independently hydrogen, halogen, NO_2 , CN or $\text{C}_1\text{-C}_4$ alkyl optionally substituted with one or more halogen atoms;

R_5 and R_6 are taken together with the atoms to which they are attached to form a 5- or 6-membered heterocyclic ring containing 1 or 2 oxygen atoms and optionally substituted with one or more halogen atoms or $\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms;

Y is hydrogen, Cl, Br, CN, NO_2 , $\text{S(O)}_n\text{T}$, Q,

$\text{C}_1\text{-C}_4$ alkyl substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or

$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, Cl, Br, $\text{S(O)}_n\text{T}$ or $\text{C}_1\text{-C}_4$ alkyl substituted with one or more halogen atoms;

T is $\text{C}_1\text{-C}_4$ alkyl substituted with one or more halogen atoms;

n is an integer of 0, 1 or 2;

R is A, OA or CN;

A is hydrogen, CR_7 , $\text{CHR}_8\text{NHCR}_9$, CH_2SO_1 ,

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C_1-C_6 alkyl optionally substituted with one to three halogen atoms,
one tri(C_1-C_4 alkyl)silyl,
one hydroxy,
one cyano,
one or two C_1-C_4 alkoxy groups optionally substituted with one to three halogen atoms,
one C_1-C_4 alkylthio,
one phenyl optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
one phenoxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
one C_1-C_6 alkoxycarbonyl group optionally



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substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or

one benzylcarbonyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,

C_3-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group, or

C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group;

R_7 is C_1-C_6 alkyl or C_3-C_6 cycloalkyl each optionally substituted with one to three halogen atoms, one hydroxy, one cyano, one or two C_1-C_4 alkoxy groups optionally substituted with one to three halogen atoms, one C_1-C_4 alkylthio, one phenyl group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups, one phenoxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups, one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups, one C_1-C_6 alkylcarbonyloxy group optionally



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substituted with one to three halogen atoms,
one C₂-C₆ alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C₁-C₄ alkyl groups or one to three C₁-C₄ alkoxy groups,
one C₁-C₆ alkoxy carbonyl group optionally substituted with one to three halogen atoms or one to three C₁-C₄ alkoxy groups, or
one benzyloxycarbonyl group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C₁-C₄ alkyl groups or one to three C₁-C₄ alkoxy groups,
C₂-C₆ alkenyl optionally substituted with one to three halogen atoms or one phenyl group,
C₃-C₆ alkynyl optionally substituted with one to three halogen atoms or one phenyl group,
phenyl optionally substituted with one or more halogen atoms, C₁-C₄ alkyl groups, C₁-C₄ alkoxy groups, phenoxy groups, C₁-C₄ alkylthio groups, tri(C₁-C₄ alkyl)silyl groups, C₁-C₄ alkylsulfinyl groups, C₁-C₄ alkylsulfonyl groups, CN groups, NO₂ groups or CF₃ groups,
phenoxy optionally substituted with one or more halogen atoms, C₁-C₄ alkyl groups, C₁-C₄ alkoxy groups, C₁-C₄ alkylthio groups, tri(C₁-C₄ alkyl)silyl groups, C₁-C₄ alkylsulfinyl groups, C₁-C₄ alkylsulfonyl groups, CN groups, NO₂ groups or CF₃ groups,

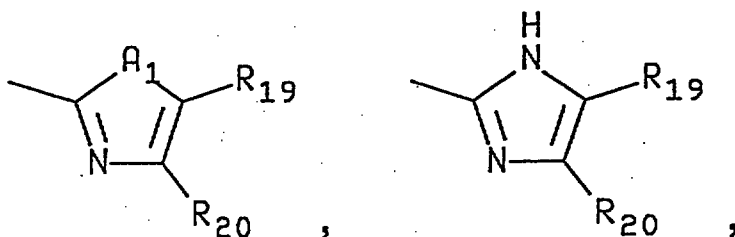


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1- or 2-naphthyl,
 2-, 3-, or 4-pyridyl optionally substituted with
 one to three halogen atoms,
 C_1-C_6 alkoxy optionally substituted with one to
 three halogen atoms, or
 C_2-C_6 alkenyloxy optionally substituted with one
 to three halogen atoms;
 R_8 is hydrogen or C_1-C_4 alkyl;
 R_9 is C_1-C_6 alkyl optionally substituted with one to
 three halogen atoms,
 phenyl optionally substituted with one to three
 halogen atoms, CN groups, NO_2 groups, C_1-C_4
 alkyl groups, C_1-C_4 alkoxy groups or CF_3
 groups,
 2- or 3-thienyl, or
 2- or 3-furyl;

Q_1 is $\begin{array}{c} A_1 \\ || \\ C-R_{10} \end{array}$, $\begin{array}{c} A_1 \\ || \\ C-OR_{11} \end{array}$, $\begin{array}{c} A_1 \\ || \\ C-NR_{12}R_{13} \end{array}$, $\begin{array}{c} A_1 \\ || \\ P(OR_{14})_2 \end{array}$, $\begin{array}{c} NR_{15} \\ || \\ C-NR_{16}R_{17} \end{array}$,
 $\begin{array}{c} NR_{15} \\ || \\ C-A_1R_{18} \end{array}$,



CN,
 C_1-C_6 alkyl optionally substituted with one or
 more halogen atoms, CN groups or phenyl
 groups, or
 phenyl optionally substituted with one or more
 halogen atoms, C_1-C_4 alkyl groups, C_1-C_4
 alkoxy groups, CN groups, NO_2 groups, CF_3
 groups or $NR_{21}R_{22}$ groups;

A_1 is O or S;

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- R_{10} is C_1-C_6 alkyl or phenyl;
 R_{11} is C_1-C_6 alkyl;
 R_{12} and R_{13} are each independently hydrogen, C_1-C_6 alkyl or may be taken together with the atom to which they are attached to form a 5- to 7-membered ring;
 R_{14} is C_1-C_4 alkyl;
 R_{15} is hydrogen, C_1-C_4 alkyl or may be taken together with either R_{16} or R_{18} and the atoms to which they are attached to form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;
 R_{16} and R_{17} are each independently hydrogen or C_1-C_4 alkyl;
 R_{18} is C_1-C_4 alkyl or when taken together with R_{15} and the atoms to which they are attached may form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;
 R_{19} and R_{20} are each independently hydrogen or C_1-C_4 alkyl or when taken together may form a ring wherein $R_{19}R_{20}$ is represented by $-CH=CH-CH=CH-$; and
 R_{21} and R_{22} are each independently hydrogen or C_1-C_4 alkyl;

with the proviso that when W is on the 3-position of the pyrrole ring, X is on the 4-position of the pyrrole ring, and Y, Z and R are each hydrogen, then X is other than 2- or 3-chlorophenyl; and with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H; and with the further proviso that when R_1 and R_2 are both H, then X and Y are other than phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

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C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms.

2. The compound according to claim 1
wherein

$\begin{array}{c} S \\ || \\ W \text{ is } CNR_1R_2; \end{array}$

R_1 and R_2 are each independently hydrogen or C_1-C_4 alkyl;

X is Q or phenyl optionally substituted with one or more halogen atoms,

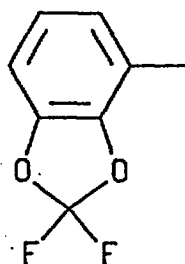
NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Q is



Y is hydrogen, Cl, Br, CN, NO_2 or CF_3 ;

Z is hydrogen, Cl, Br or CF_3 ;

R is A or CN;

$\begin{array}{c} O \\ || \\ A \text{ is hydrogen, } CR_7 \text{ or} \end{array}$

C_1-C_6 alkyl optionally substituted with one to three halogen atoms,

one C_1-C_4 alkoxy group,

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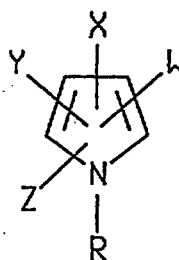


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one cyano,
 one C_1-C_6 alkylcarbonyloxy group,
 one benzylcarbonyloxy group, or
 one phenylcarbonyloxy group optionally substituted with one to three halogen atoms or one C_1-C_4 alkyl group; and
 R_7 is phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO_2 groups or CF_3 groups.

3. The compound according to claim 2 selected from the group consisting of 4-cyanopyrrole-2-thiocarboxamide; 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-thiocarboxamide; 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N-methyl-5-(trifluoromethyl)pyrrole-3-thiocarboxamide; and 4-(2,3-dichlorophenyl)pyrrole-3-thiocarboxamide.

4. A method for controlling insects and acarina which comprises contacting said insects and acarina, their breeding grounds, food supply or habitat with an insecticidally or acaricidally effective amount of a compound having the structural formula



wherein

$\begin{array}{c} S \\ || \\ W \end{array}$ is CNR_1R_2 ;

R_1 and R_2 are each independently hydrogen,

C_1-C_4 alkyl optionally substituted with one or



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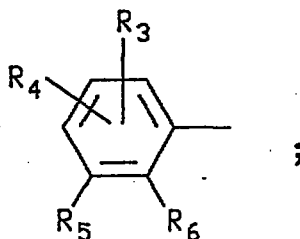
phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

X is Cl, Br, CN, NO₂, Q,

C₁-C₄ alkyl substituted with one or more halogen
atoms, or

phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

Q is



R₃ and R₄ are each independently hydrogen, halogen,
NO₂, CN or C₁-C₄ alkyl optionally substituted with
one or more halogen atoms;

R₅ and R₆ are taken together with the atoms to which
they are attached to form a 5- or 6-membered
heterocyclic ring containing 1 or 2 oxygen atoms
and optionally substituted with one or more
halogen atoms or C₁-C₄ alkyl groups optionally
substituted with one or more halogen atoms;



Y is hydrogen, Cl, Br, CN, NO₂, S(O)_nT, Q,
C₁-C₄ alkyl substituted with one or more halogen
atoms, or
phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;
Z is hydrogen, Cl, Br, S(O)_nT or C₁-C₄ alkyl substi-
tuted with one or more halogen atoms;
T is C₁-C₄ alkyl substituted with one or more halogen
atoms;
n is an integer of 0, 1 or 2;
R is A, OA or CN;

A is hydrogen, $\begin{array}{c} \text{O} \\ \parallel \\ \text{CR}_7 \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ \text{CHR}_8\text{NHCR}_9 \end{array}$, CH₂SO₁,
C₁-C₆ alkyl optionally substituted with one to
three halogen atoms,
one tri(C₁-C₄ alkyl)silyl,
one hydroxy,
one cyano,
one or two C₁-C₄ alkoxy groups optionally
substituted with one to three halogen
atoms,
one C₁-C₄ alkylthio,
one phenyl optionally substituted with one to
three halogen atoms, one to three C₁-C₄
alkyl groups or one to three C₁-C₄
alkoxy groups,
one phenoxy group optionally substituted with

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- one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
 - one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
 - one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
 - one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
 - one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
 - one C_1-C_6 alkoxy carbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or
 - one benzylcarbonyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
 - C_3-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group, or
 - C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group;
- R_7 is C_1-C_6 alkyl or C_3-C_6 cycloalkyl each optionally substituted with one to three halogen atoms, one hydroxy, one cyano,

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- one or two C_1-C_4 alkoxy groups optionally substituted with one to three halogen atoms,
- one C_1-C_4 alkylthio,
- one phenyl group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one phenoxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one benzyloxy group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one C_1-C_6 alkylcarbonyloxy group optionally substituted with one to three halogen atoms,
- one C_2-C_6 alkenylcarbonyloxy group optionally substituted with one to three halogen atoms,
- one phenylcarbonyloxy group optionally substituted with one to three halogen atoms, one to three C_1-C_4 alkyl groups or one to three C_1-C_4 alkoxy groups,
- one C_1-C_6 alkoxycarbonyl group optionally substituted with one to three halogen atoms or one to three C_1-C_4 alkoxy groups, or
- one benzyloxycarbonyl group optionally substituted on the phenyl ring with one to three halogen atoms, one to three C_1-C_4



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alkyl groups or one to three C_1-C_4 alkoxy groups,

C_2-C_6 alkenyl optionally substituted with one to three halogen atoms or one phenyl group,

C_3-C_6 alkynyl optionally substituted with one to three halogen atoms or one phenyl group,

phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, phenoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,

phenoxy optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, C_1-C_4 alkylthio groups, tri(C_1-C_4 alkyl)silyl groups, C_1-C_4 alkylsulfinyl groups, C_1-C_4 alkylsulfonyl groups, CN groups, NO_2 groups or CF_3 groups,

1- or 2-naphthyl,

2-, 3-, or 4-pyridyl optionally substituted with one to three halogen atoms,

C_1-C_6 alkoxy optionally substituted with one to three halogen atoms, or

C_2-C_6 alkenyloxy optionally substituted with one to three halogen atoms;

R_8 is hydrogen or C_1-C_4 alkyl;

R_9 is C_1-C_6 alkyl optionally substituted with one to three halogen atoms,

phenyl optionally substituted with one to three halogen atoms, CN groups, NO_2 groups, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups or CF_3 groups,

2- or 3-thienyl, or

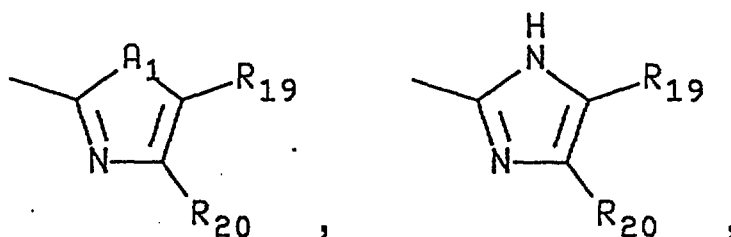
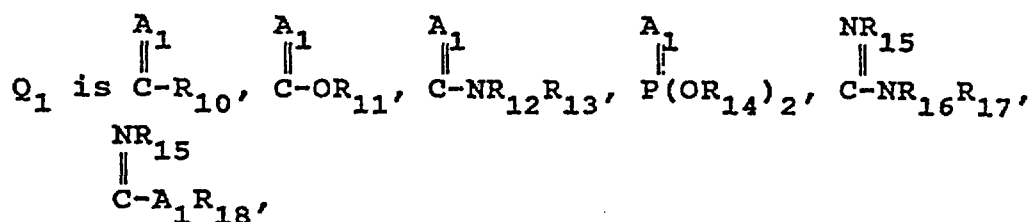
2- or 3-furyl;



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CN,

C_1-C_6 alkyl optionally substituted with one or more halogen atoms, CN groups or phenyl groups, or

phenyl optionally substituted with one or more halogen atoms, C_1-C_4 alkyl groups, C_1-C_4 alkoxy groups, CN groups, NO_2 groups, CF_3 groups or $NR_{21}R_{22}$ groups;

A_1 is O or S;

R_{10} is C_1-C_6 alkyl or phenyl;

R_{11} is C_1-C_6 alkyl;

R_{12} and R_{13} are each independently hydrogen, C_1-C_6 alkyl or may be taken together with the atom to which they are attached to form a 5- to 7-membered ring;

R_{14} is C_1-C_4 alkyl;

R_{15} is hydrogen, C_1-C_4 alkyl or may be taken together with either R_{16} or R_{18} and the atoms to which they are attached to form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

R_{16} and R_{17} are each independently hydrogen or C_1-C_4 alkyl;

R_{18} is C_1-C_4 alkyl or when taken together with R_{15} and



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the atoms to which they are attached may form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

R_{19} and R_{20} are each independently hydrogen or C_1-C_4 alkyl or when taken together may form a ring wherein $R_{19}R_{20}$ is represented by $-CH=CH-CH=CH-$; and

R_{21} and R_{22} are each independently hydrogen or C_1-C_4 alkyl;

with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.

5. The method according to claim 4

wherein

$\begin{array}{c} S \\ || \\ W \text{ is } CNR_1R_2; \end{array}$

R_1 and R_2 are each independently hydrogen or C_1-C_4 alkyl;

X is Q or phenyl optionally substituted with one or more halogen atoms,

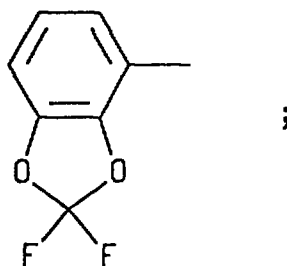
NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Q is



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Y is hydrogen, Cl, Br, CN, NO₂ or CF₃;

Z is hydrogen, Cl, Br or CF₃;

R is A or CN;

A is hydrogen, $\overset{\text{O}}{\parallel}\text{CR}_7$ or

C₁-C₆ alkyl optionally substituted with one to three halogen atoms,

one C₁-C₄ alkoxy group,

one cyano,

one C₁-C₆ alkylcarbonyloxy group,

one benzylcarbonyloxy group, or

one phenylcarbonyloxy group optionally sub-

stituted with one to three halogen atoms

or one C₁-C₄ alkyl group; and

R₇ is phenyl optionally substituted with one or more

halogen atoms, C₁-C₄ alkyl groups, C₁-C₄ alkoxy groups, CN groups, NO₂ groups or CF₃ groups.

6. The method according to claim 5 wherein the compound is selected from the group consisting of 4-cyanopyrrole-2-thiocarboxamide; 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-thiocarboxamide; 4-bromo-2-(p-chlorophenyl)-1-(ethoxymethyl)-N-methyl-5-(trifluoromethyl)pyrrole-3-thiocarboxamide; and 4-(2,3-dichlorophenyl)pyrrole-3-thiocarboxamide.

7. The method according to claim 4 further comprising the simultaneous or sequential addition of an insecticidally or acaricidally effective amount of one or more other biological chemicals.

8. A method for protecting growing plants from attack by insects and acarina which comprises

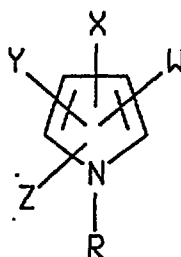
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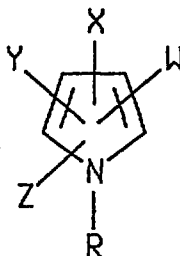
applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally or acaricidally effective amount of a compound having the structural formula



wherein W, X, Y, Z and R are as described in claim 4.

9. The method according to claim 8 wherein the compound is applied to the plants or soil in which they are growing at a rate of about 0.100 kg/ha to 4.0 kg/ha.

10. A composition for controlling insects and acarina comprising an agronomically acceptable carrier and an insecticidally or acaricidally effective amount of a compound having the structural formula



wherein W, X, Y, Z and R are as described in claim 1.



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PYRROLE THIOCARBOXAMIDE INSECTICIDAL AND
ACARICIDAL AGENTS

ABSTRACT OF THE INVENTION

There are provided pyrrole thiocarboxamide compounds which are useful for the control of insects and acarina. Further provided are compositions and methods comprising those compounds for the protection of plants from attack by insects and acarina.

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REPLACEMENT SHEETS		SG
☒	Description : paged 014, 211 to paged -	
☒	Claim(s) : paged 40, 46, 47, 48, 55, 56 to paged -	
☐	Drawing(s) : paged to paged	
☐	Abstract : paged to paged	
DATE OF RECEIPT 15/1/99		

**PYRROLE THIOCARBOXAMIDE INSECTICIDAL
AND ACARICIDAL AGENTS**

In spite of the commercial insecticides and acaricides available today, damage to crops, both growing and harvested, caused by insects and acarina still occurs. Accordingly, there is ongoing research to create new and more effective insecticides and acaricides.

FR 2,569,189 describes certain pesticidal pyrrole derivatives which are linked to a pyrethroid acid derivative through an ester group.

EP-A-347 488 describes arylpyrrole insecticidal, acaricidal and nematocidal agents. However, that application does not disclose any thiocarboxamide substituted pyrroles.

EP-A-372 982 and EP-A-460 940 disclose substituted 1-arylpyrrole insecticidal, acaricidal and nematocidal agents. However, those applications do not describe any thiocarboxamide substituted pyrroles. In addition, those applications only disclose 1-arylpyrrole compounds. In contrast, the present invention does not describe any 1-arylpyrrole compounds.

EP-A-243 014 describes acrylic acid derivatives which are useful as fungicides, insecticides and plant growth regulators. However, that application does not disclose any thiocarboxamide substituted pyrroles.

Further pyrrole derivatives which are excluded from the current invention on account of the provisos or on account of the X substituent are known from CA64:3571g, US3393201 and Nyfeler & Ackermann, Synthesis & Chemistry of Agrochemicals, Baker et al Editors, ACS, Washington 1992, chapter 36.

It is therefore an object of the present invention to provide pyrrole thiocarboxamide compounds which are highly effective for controlling insects and acarina.

It is also an object of the present invention to provide a method for protecting growing plants from attack by insects and acarina by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally or acaricidally effective amount of a pyrrole thiocarboxamide compound.

These and other objects of the present invention will become more apparent from the detailed description thereof set forth below.

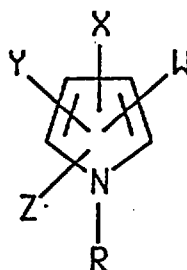
The present invention describes pyrrole thiocarboxamide compounds which are highly effective insecticidal and acaricidal agents useful for the control of insect and acarid pests and for protecting agronomic crops from attack by said pests.

This invention also relates to insecticidal and acaricidal compositions containing those compounds

and methods for using those compounds and compositions for the control of insects and acarina and for the protection of growing or harvested plants from attack by insects and acarina.

5 The insecticidal and acaricidal pyrrole thiocarboxamide compounds of the present invention have the following structural formula I:

10



15

wherein

$$\begin{array}{c} \text{S} \\ || \\ \text{W is CNR}_1\text{R}_2; \end{array}$$

R_1 and R_2 are each independently hydrogen,

20

$\text{C}_1\text{-C}_4$ alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

25

$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or

$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;

X is O,

30

or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

35

CN groups,

R is hydrogen or C₁-C₆ alkyl substituted with one C₁-C₄ alkoxy group.

5 The present invention also relates to novel pyrrole thiocarboxamide compounds having the structural formula



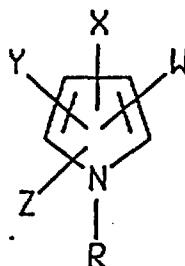
15 wherein W, X, Y, Z and R are as described hereinabove for formula I with the proviso that when W is on the 3-position of the pyrrole ring and X is on the 4-position of the pyrrole ring and Y, Z and R are each hydrogen, then X is other than 2- or 3-chlorophenyl;
20 and with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.

Exemplary of halogen hereinabove are fluorine, chlorine, bromine and iodine.

Advantageously, the present invention provides a method for controlling insects and acarina by
35 contacting said insects and acarina, their breeding

CLAIM:

1. A compound having the structural formula



wherein

W is CNR_1R_2 ;

R_1 and R_2 are each independently hydrogen,

$\text{C}_1\text{-C}_4$ alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or

$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;

X is Q,

or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or

$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;



R_{10} is C_1-C_6 alkyl or phenyl;

R_{11} is C_1-C_6 alkyl;

R_{12} and R_{13} are each independently hydrogen, C_1-C_6 alkyl or may be taken together with the atom to which they are attached to form a 5- to 7-membered ring;

R_{14} is C_1-C_4 alkyl;

R_{15} is hydrogen, C_1-C_4 alkyl or may be taken together with either R_{16} or R_{18} and the atoms to which they are attached to form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

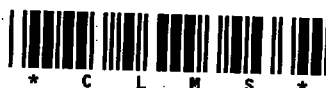
R_{16} and R_{17} are each independently hydrogen or C_1-C_4 alkyl;

R_{18} is C_1-C_4 alkyl or when taken together with R_{15} and the atoms to which they are attached may form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

R_{19} and R_{20} are each independently hydrogen or C_1-C_4 alkyl or when taken together may form a ring wherein $R_{19}R_{20}$ is represented by $-CH=CH-CH=CH-$; and

R_{21} and R_{22} are each independently hydrogen or C_1-C_4 alkyl;

with the proviso that when W is on the 3-position of the pyrrole ring, X is on the 4-position of the pyrrole ring, and Y, Z and R are each hydrogen, then X is other than 2- or 3-chlorophenyl; and with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.



2. The compound according to claim 1
wherein

$\begin{array}{c} \text{S} \\ || \\ \text{W is } \text{CNR}_1\text{R}_2; \end{array}$

R_1 and R_2 are each independently hydrogen or $\text{C}_1\text{-C}_4$ alkyl;

X is Q or phenyl optionally substituted with one or more halogen atoms,

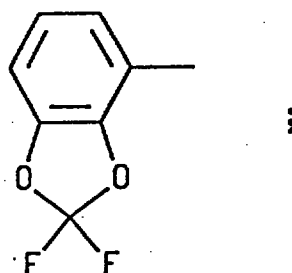
NO_2 groups,

CN groups,

$\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or

$\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;

Q is



Y is hydrogen, Cl , Br , CN , NO_2 or CF_3 ;

Z is hydrogen, Cl , Br or CF_3 ;

R is A or CN ;

$\begin{array}{c} \text{O} \\ || \\ \text{A is hydrogen, CR}_7 \text{ or} \end{array}$

$\text{C}_1\text{-C}_6$ alkyl optionally substituted with one to three halogen atoms,

one $\text{C}_1\text{-C}_4$ alkoxy group,



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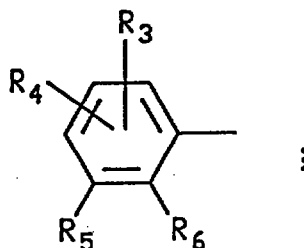
phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

X is Q,

or

phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

Q is



R₃ and R₄ are each independently hydrogen, halogen,
NO₂, CN or C₁-C₄ alkyl optionally substituted with
one or more halogen atoms;

R₅ and R₆ are taken together with the atoms to which
they are attached to form a 5- or 6-membered
heterocyclic ring containing 1 or 2 oxygen atoms
and optionally substituted with one or more
halogen atoms or C₁-C₄ alkyl groups optionally
substituted with one or more halogen atoms;



the atoms to which they are attached may form a 5- to 7-membered ring optionally substituted with one or two C_1-C_4 alkyl groups;

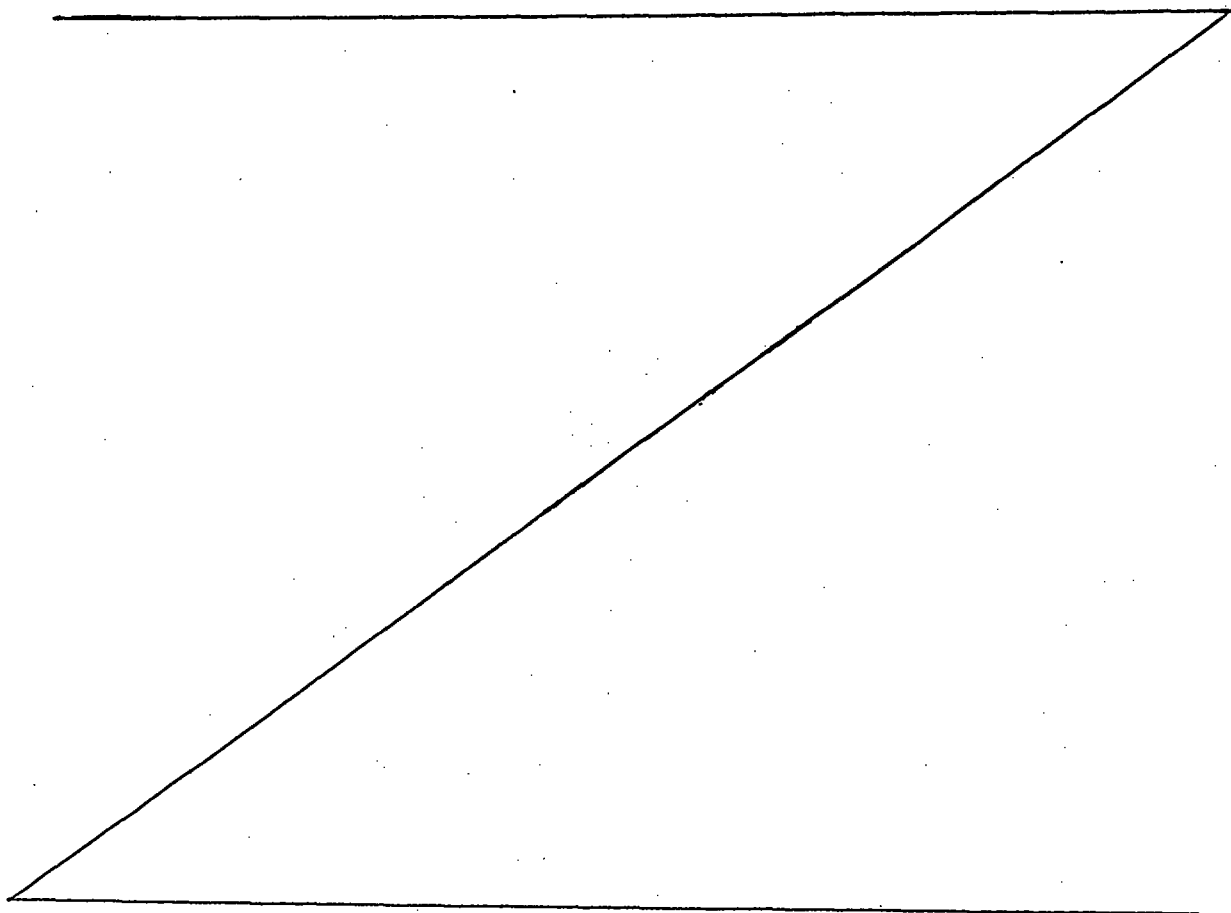
R_{19} and R_{20} are each independently hydrogen or C_1-C_4 alkyl or when taken together may form a ring wherein $R_{19}R_{20}$ is represented by $-CH=CH-CH=CH-$; and

R_{21} and R_{22} are each independently hydrogen or C_1-C_4 alkyl;

with the proviso that when W is on the 2- or 5-position of the pyrrole ring, then R is other than H.

5. The method according to claim 4

wherein the compound is a compound as defined by Claim 2.



6. The method according to Claim 5 wherein the compound is a compound as defined by Claim 3.

7. The method according to claim 4 further comprising the simultaneous or sequential addition of an insecticidally or acaricidally effective amount of one or more other biological chemicals.

8. A method for protecting growing plants from attack by insects and acarina which comprises

