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(71) Applicant: *(for all designated States except US):* DUNLENA PTY. LTD. [AU/AU]; 168 Walker Street, North Sydney, NSW 2060 (AU).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)* : LAHM, George, Philip [US/US]; 148 Fairhill Drive, Wilmington, DE 19808 (US).

(74) Agents: COSTELLO, James, A. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

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(54) Title: ARTHROPODICIDAL ARYL SULFONATES

(57) Abstract

Arthropodicidal aryl sulfonates of the formula R^1-SO_2-O-Q, wherein R^1 and Q are as defined in the text, Q being meta-substituted by the described sulfur-containing moieties.

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TITLE

ARTHROPODICIDAL ARYL SULFONATES

The aryl sulfonates of this invention are characterized by aryl and heteroaryl rings containing substituted alkylthio, alkylsulfinyl or alkylsulfonyl groups. These substituted groups distinguish the compounds of this invention from the aryl sulfonates of U.S. 4,791,127, U.S. 4,652,574 and U.S. 3,818,102.

SUMMARY OF THE INVENTION

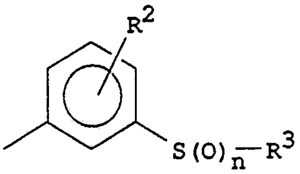
This invention pertains to compounds of Formula I, including all geometric and stereoisomers, agriculturally suitable salts thereof, agricultural compositions containing them and their use for the control of arthropods and nematodes in both agronomic and nonagronomic environments. The compounds are

$$R^1—SO_2—O—Q$$

I

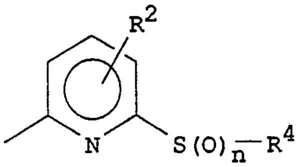
wherein:

Q is selected from the group



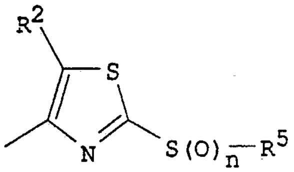
Q-1

,



Q-2

and



Q-3

;

R^1 is selected from the group C_1-C_3 alkyl and C_1-C_3 haloalkyl;

R^2 is selected from the group H, C_1-C_2 alkyl, C_1-C_2 haloalkyl, C_1-C_2 alkoxy, C_1-C_2 haloalkoxy, C_1-C_2 alkylthio, C_1-C_2 haloalkylthio, C_1-C_2 alkylsulfinyl, C_1-C_2 haloalkylsulfinyl, C_1-C_2 alkylsulfonyl, C_1-C_2 haloalkylsulfonyl, amino, C_1-C_2 alkylamino, C_2-C_4 dialkylamino, C_2-C_3 alkoxycarbonyl; phenyl optionally substituted with halogen, CN or NO_2; halogen; NO_2; and CN;

R^3 is selected from the group C_1-C_6 alkyl substituted with R^6, C_3-C_6 alkenyl substituted with R^6, C_3-C_6 alkynyl substituted with R^7 and C_4-C_7 cycloalkylalkyl optionally substituted with R^8; wherein when R^3 is C_3-C_6 alkenyl substituted with R^7 and R^7 is 1 to 3 halogens, then n is 0 or 1;

R^4 and R^5 are independently selected from the group C_1-C_6 alkyl substituted with R^9, C_2-C_6 alkenyl substituted with R^{10}, and C_2-C_6 alkynyl substituted with R^{10};

R^6 is selected from the group CN, SCN, NO_2, OH, OR^{11}, SR^{11}, $S(O)R^{11}$, SO_2R^{11}, $OC(O)R^{11}$, OSO_2R^{11}, $Si(R^{11})(R^{12})(R^{13})$, CO_2R^{11}, $C(O)N(R^{11})R^{12}$, $C(O)R^{11}$ and $N(R^{11})R^{12}$;

R^7 is selected from the group 1-3 halogens, C_1-C_3 alkyl, CN, SCN, NO_2, OH, OR^{11}, SR^{11}, $S(O)R^{11}$, SO_2R^{11}, $OC(O)R^{11}$, OSO_2R^{11}, $Si(R^{11})(R^{12})(R^{13})$, CO_2R^{11}, $C(O)N(R^{11})R^{12}$, $C(O)R^{11}$ and $N(R^{11})R^{12}$;

R^8 is selected from the group 1-3 halogens, CN and C_1-C_2 alkyl;

R^9 is selected from the group CN, SCN, NO_2, OH, OR^{14}, SR^{14}, $S(O)R^{11}$, SO_2R^{11}, $OC(O)R^{11}$, OSO_2R^{11}, $Si(R^{11})(R^{12})(R^{13})$, CO_2R^{11}, $C(O)N(R^{11})R^{12}$, $C(O)R^{11}$ and $N(R^{11})R^{12}$;

R^{10} is selected from the group 1-3 halogens, C_1-C_3 alkyl, CN, SCN, NO_2, OH, OR^{11}, SR^{11}, $S(O)R^{11}$, SO_2R^{11}, $OC(O)R^{11}$, OSO_2R^{11}, $Si(R^{11})(R^{12})(R^{13})$, CO_2R^{11}, $C(O)N(R^{11})R^{12}$, $C(O)R^{11}$ and $N(R^{11})R^{12}$;

R^{11}, R^{12} and R^{13} are independently selected from the group C_1-C_3 alkyl and C_1-C_3 haloalkyl;

R^{14} is selected from C_1-C_3 haloalkyl; and

n is 0, 1 or 2.

Preferred Compounds A are compounds of Formula I wherein:

R^1 is CH_3;

R^2 is selected from the group H, CH_3, halogen, CF_3 and CN;

R^6 is selected from the group CN, SCN, $Si(R^{11})(R^{12})(R^{13})$, OR^{11} and SR^{11};

R^7 is selected from the group 1-3 halogens, CN, SCN, $Si(R^{11})(R^{12})(R^{13})$, OR^{11} and SR^{11};

R^9 is selected from the group CN, SCN, $Si(R^{11})(R^{12})(R^{13})$, OR^{14} and SR^{14}; and

R^{10} is selected from the group 1-3 halogens, CN, SCN, $Si(R^{11})(R^{12})(R^{13})$, OR^{11} and SR^{11}.

Preferred Compounds B are compounds of Preferred A wherein Q is Q-1. Preferred Compounds C are compounds of Preferred A wherein Q is Q-2. Preferred Compounds D are compounds of Preferred A wherein Q is Q-3.

Some of the compounds of this invention can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active than the others and how to separate said stereoisomers. Accordingly, the present invention comprises racemic mixtures, individual stereoisomers, and optically active mixtures of compounds of Formula I as well as agriculturally suitable salts thereof.

In the above recitations, the term "alkyl" used either alone or in compound word such as "haloalkyl", denotes straight or branched alkyl such as methyl, ethyl, n-propyl, isopropyl, or the different butyl, pentyl or hexyl isomers. Alkoxy denotes methoxy and ethoxy. Alkenyl denotes straight or branched chain alkenes such as vinyl, 1-propenyl, 2-propenyl, 3-propenyl and the different butenyl, pentenyl and hexenyl isomers. Alkynyl denotes straight chain or branched alkynes such as ethynyl, 1-propynyl, 3-propynyl and the different butynyl, pentynyl and hexynyl isomers. Cycloalkylalkyl denotes cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl attached to a straight or branched C_1–C_4 alkylene group.

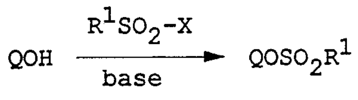
The term "halogen", either alone or in compound words such as "haloalkyl", denotes fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl" said alkyl may be partially or fully substituted with halogen atoms, which may be the same or different. Examples of haloalkyl include CH_2CH_2F, CF_2CF_3 and CH_2CHFCl. The terms "haloalkenyl" and "haloalkynyl" are defined analogously to the term "haloalkyl".

The total number of carbon atoms in a substituent group is indicated by the "C_i-C_j" prefix where i and j are numbers from 1 to 7. For example, C_2 alkoxycarbonyl designates $C(O)OCH_3$ and C_3 alkoxycarbonyl designates $C(O)OCH_2CH_3$.

DETAILS OF THE INVENTION

Compounds of Formula I can be prepared by the reaction of hydroxyaryl compounds of Formula II with an alkylsulfonylating reagent such as an alkylsulfonyl halide or an alkylsulfonic acid anhydride. This reaction is generally conducted in a solvent and typically employs a base to initiate the reaction and quench the liberated acid by-product. Suitable solvents include, tetrahydrofuran, diethyl ether, methylene chloride, chloroform, benzene and toluene. Examples of typical bases include triethylamine and pyridine. The reactions are usually run at temperatures in the range of about 0° to 30°C. This reaction is depicted in Scheme 1.

Scheme 1

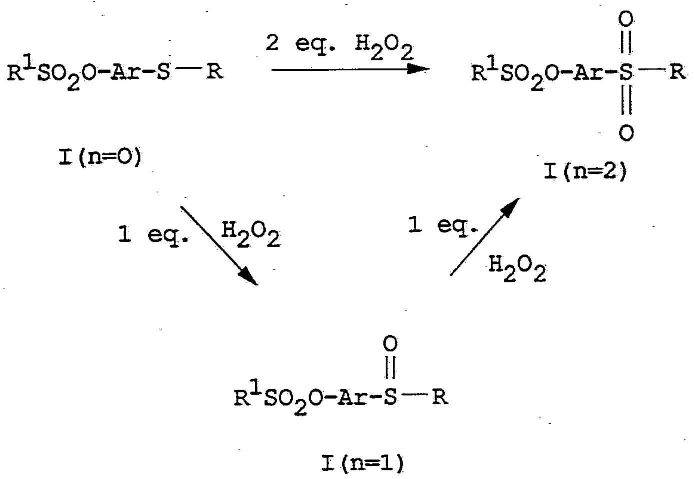


$$\underset{\text{II}}{QOH} \xrightarrow[\text{base}]{R^1SO_2\text{-}X} \underset{\text{I}}{QOSO_2R^1}$$

$X = Cl$ or OSO_2R^1

The sulfoxide (I, n=1) and sulfone (I, n=2) derivatives of Formula I are generally prepared from the sulfide derivatives (I, n=0). Oxidation to the sulfoxide can be achieved with a variety of oxidative reagents such as hydrogen peroxide, m-chloroperbenzoic acid, sodium periodate and t-butylhypochlorite. To minimize or prevent over oxidation, stoichiometric amounts of the oxidative reagent can be employed. For example, one equivalent of 30% hydrogen peroxide at room temperature is usually sufficient to convert a sulfide to a sulfoxide. Sulfoxides can be further oxidized to the sulfone by an additional equivalent of 30% hydrogen peroxide and may require higher temperatures. Other reagents for the oxidation of sulfoxides to sulfones include potassium permanganate and peracetic acid. In the presence of sufficient oxidizing agent, sulfides can be directly oxidized to the sulfone. Scheme 2 depicts these transformations.

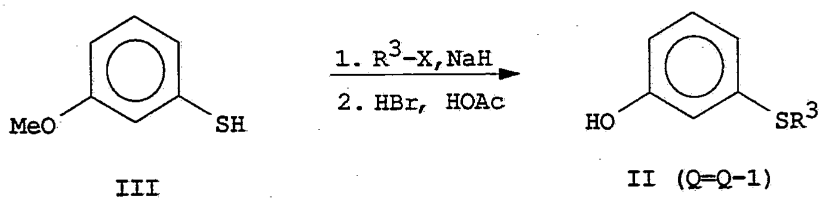
Scheme 2



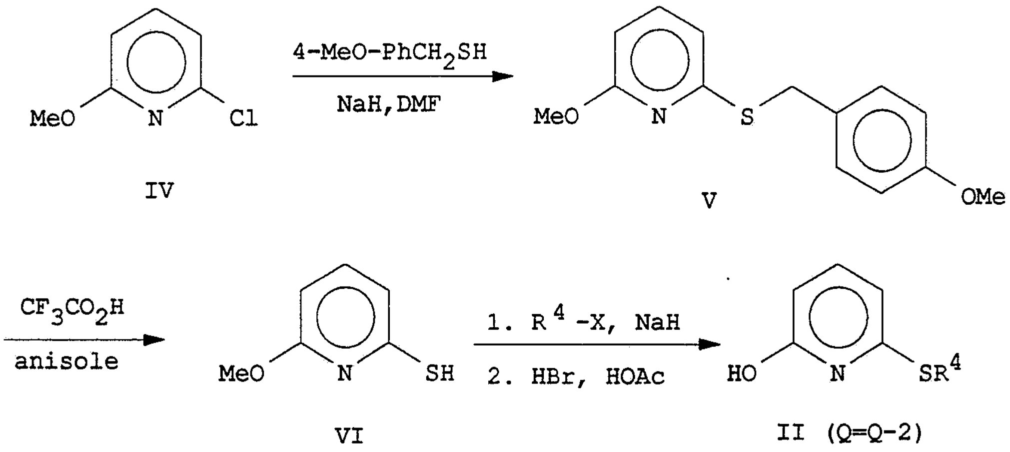
Ar = benzene, pyridine, thiazole; R = R^3, R^4, R^5

Intermediate hydroxyaryl compounds of Formula II can be prepared as depicted in Schemes 3, 4 and 5. The key step in the synthesis of each of these intermediates is the alkylation of an aryl or heteroaryl mercaptan (III, VI and VII) with a substituted alkyl, alkenyl or alkynyl halide (i.e. R^3X, R^4X and R^5X) where X is a halogen leaving group such as chlorine, bromine or iodine.

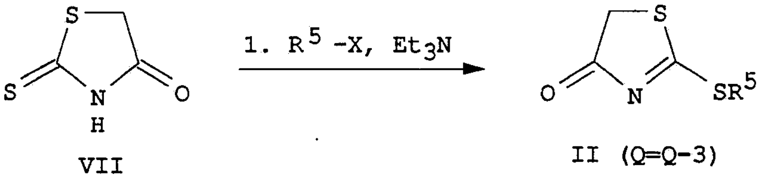
Scheme 3



Scheme 4



Scheme 5



EXAMPLE 1

6-[[(Trimethylsilyl)methyl]thio]-2-pyridinol methanesulfonate (ester)

Step A: 2-Methoxy-6-[[(4-methoxyphenyl)methyl]thio]-pyridine

To a mixture of 60% sodium hydride (25.9 g, 0.648 mol) in 400 mL of dimethylformamide was added a mixture of 4-methoxy-α-toluenethiol (100 g, 0.648 mol) in 100 mL of dimethylformamide at a rate that produced a slow evolution of hydrogen. Once the addition was complete, 2-chloro-6-methoxy pyridine was added in one portion and the mixture was heated at 70°C overnight. The mixture was then partitioned between 5% aqueous sodium bicarbonate and ether. The ether extracts were dried over magnesium sulfate and concentrated.

Distillation of the crude product afforded 71.28 g of a fraction boiling at 148-183°C which consisted primarily of the title compound by NMR. ^{1}H NMR ($CDCl_3$) δ 3.78 (s,3H), 3.95 (s,3H), 4.39 (s,2H), 6.44 (d,1H), 6.76 (d,1H), 6.83 (d,2H), 7.3-7.5 (m,4H).

Step B: 6-Methoxy-2-pyridinethiol

A mixture of 2-methoxy-6-[[(4-methoxyphenyl)methyl]-thio]pyridine (71.28 g, 0.273 mol), anisole (35.2 mL, 0.328 mol) and 300 mL of trifluoroacetic acid was heated at reflux, under nitrogen, for 3 days. After this time, the trifluoroacetic acid was removed on a rotary evaporator, 1000 mL of 10% sodium acetate was added, and the mixture was extracted with chloroform. The aqueous phase was then washed twice with ethyl acetate, the chloroform and ethyl acetate extracts were combined, dried over magnesium sulfate and concentrated. Trituration of the crude product with ether afforded 24.94 g of the product as a light yellow solid, mp 129-132°C. ^{1}H NMR ($CDCl_3$) δ 3.91 (s,3H), 6.37 (d,1H), 6.85 (d,1H), 7.38 (t,1H).

Step C: 2-Methoxy-6-[[(trimethylsilyl)methyl]thio]-pyridine

A mixture of 6-methoxy-2-pyridinethiol (1.5 g, 10.6 mmol), potassium carbonate (2.6 g, 19.1 mmol) and chloromethyltrimethylsilane (1.7 g, 13.8 mmol) in 25 mL of dimethylformamide was heated at 60°C overnight. The reaction was cooled to room temperature and partitioned between ether and 5% aqueous sodium bicarbonate, the ether extracts were washed with water, dried over magnesium sulfate and concentrated. Chromatography on silica gel (95:5 hexane:ethyl acetate) afforded 1.72 g of product as a clear, colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.15 (s,9H), 2.35 (s,2H), 3.94 (s,3H), 6.40 (d,1H), 6.78 (d,1H), 7.38 (t,1H).

Step D: 6-[[(trimethylsilyl)methyl]thio]-2-pyridinol methanesulfonate (ester)

A mixture of 2-methoxy-6-[[(trimethylsilyl)methyl]thio]pyridine (0.75 g, 3.30 mmol) in 3.0 mL of acetic acid and 1.2 mL of of 48% HBr was heated at reflux under nitrogen for 2 hours. After this time, the reaction was diluted with toluene and concentrated. To the crude product was added 5 mL of water and then 1N sodium hyroxide until a pH of greater than 7 was reached. Then, 1N hydrochloric acid was added until pH 4 was achieved. Ethyl acetate was added and the mixture was stirred several minutes until a homogeneous solution was obtained. The product was extracted twice with ethyl acetate, the organic extracts were dried over magnesium sulfate and concentrated to 0.63 g of a yellow solid. The crude product was taken up in 15 mL of tetrahydrofuran and methanesulfonyl chloride (0.26 mL, 3.30 mmol) was added. After cooling to 0°C under nitrogen, triethylamine (0.55 mL, 3.63 mmol) was added and the reaction was slowly warmed to room temperature. The reaction was stirred overnight and then partitioned between methylene chloride and water, the organic extracts were dried over magnesium sulfate, and concentrated to 1.05 g of a brown oil. Chromatography on silica gel (8:2 hexane:ethyl acetate) followed by distillation with a Kugelrohr apparatus afforded 0.22 g of the title compound as a clear colorless oil which set up to a white solid, mp 59°-61°C. ^{1}H NMR ($CDCl_3$) δ 0.16 (s,9H), 2.29 (s,2H), 3.50 (s,3H), 6.77 (d,1H), 7.17 (d,1H), 7.60 (t,1H).

EXAMPLE 2

6-[(3,4,4-trifluoro-3-butenyl)thio]-2-pyridinol methanesulfonate (ester)

The procedures described in Steps B through D of Example 1 using 0.75 g of 6-methoxy-2-pyridinethiol and 1.3 g of 4-bromo-1,1,2-trifluorobutene afforded 0.94 g of the product as a clear, colorless oil which on standing set up to a white solid, mp 48°-52°C. ^{1}H NMR ($CDCl_3$) δ 2.7-2.9 (m,2H), 3.31 (t,2H), 3.44 (s,3H), 6.82 (d,1H), 7.18 (d,1H), 7.63 (t,1H).

EXAMPLE 3

6-[(3-cyanopropyl)thio]-2-pyridinol methanesulfonate (ester)

The procedures described in Steps B through D of Example 1 using 0.75 g of 6-methoxy-2-pyridinethiol and 0.72 g of 4-chlorobutyronitrile afforded 1.28 g of the product as a white solid, mp 80°-84°C. ^{1}H NMR ($CDCl_3$) δ 2.10 (m,2H), 2.54 (t,2H), 3.27 (t,2H), 3.44 (s,3H), 6.78 (d,1H), 7.16 (d,1H), 7.62 (t,1H).

EXAMPLE 4

6-[(3-cyanopropyl)sulfinyl]-2-pyridinol methanesulfonate (ester)

A mixture of 6-[(3-cyanopropyl)thio]-2-pyridinol methanesulfonate (ester) (0.75 g, 2.76 mmol), 0.5 mL of 30% hydrogen peroxide and 10 mL of acetic acid was stirred at room temperature, under nitrogen, overnight. The acetic acid was then neutralized with 5% aqueous sodium bicarbonate and the aqueous phase extracted twice with ethyl acetate. The organic extracts were dried over magnesium sulfate and concentrated. Chromatography on silica gel with ethyl acetate as eluent afforded 0.89 g of the title compound as a clear, colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.92 (m,1H), 2.35 (m,1H), 2.55 (t,2H), 3.15 (m,1H), 3.28 (m,1H), 3.48 (s,3H), 7.22 (d,1H), 7.97 (d,1H), 8.10 (t,1H).

EXAMPLE 5

6-[(3-cyanopropyl)sulfonyl]-2-pyridinol methanesulfonate (ester)

A mixture of 6-[(3-cyanopropyl)thio]-2-pyridinol methanesulfonate (ester) (0.75 g, 2.76 mmol), 1.0 mL of 30% hydrogen peroxide and 10 mL of acetic acid was heated at 90°C, under nitrogen, overnight. The acetic acid was then neutralized with 5% aqueous sodium bicarbonate and the aqueous phase extracted twice with ethyl acetate. The organic extracts were dried over magnesium sulfate and concentrated. Chromatography on silica gel (1:1 ethyl acetate:hexane) afforded 0.90 g of the title compound as a clear, colorless oil. ^1H NMR ($CDCl_3$) δ 2.12 (m,2H), 2.62 (t,2H), 3.50 (t,2H), 3.56 (s,3H), 7.40 (d,1H), 8.09 (d,1H), 8.16 (t,1H).

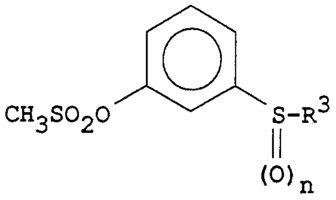
EXAMPLES 6 and 7

6-[(3,4,4-trifluoro-3-butenyl)sulfonyl]-2-pyridinol methanesulfonate (ester); and 6-[(3,4,4-trifluoro-3-butenyl)sulfinyl]-2-pyridinol methanesulfonate (ester)

A mixture of 6-[(3,4,4-trifluoro-3-butenyl)thio]-2-pyridinol methanesulfonate (ester) (0.79 g, 2.52 mmol), 0.5 mL of 30% hydrogen peroxide and 10 mL of acetic acid was stirred at room temperature, under nitrogen, for 48 hours. The acetic acid was then neutralized with saturated aqueous sodium bicarbonate and the aqueous phase extracted with ethyl acetate. The organic extracts were dried over magnesium sulfate and concentrated. Chromatography on silica gel (1:1 ethyl acetate:hexane) afforded two products. The higher Rf product (Example 6) (Rf approximately 0.6, 1:1 ethyl acetate:hexane) was determined by NMR to be the sulfonyl derivative, and the lower Rf product (Example 7) (Rf approximately 0.2, 1:1 ethyl acetate:hexane) was determined by NMR to be the sulfinyl derivative. Example 6: ^1H NMR ($CDCl_3$) δ 2.8-2.9 (m,2H), 3.54 (s,3H), 3.57, (t,2H), 7.41 (d,1H), 8.08 (d,1H), 8.15 (t,1H). Example 7: ^{1}H NMR ($CDCl_3$) δ 2.4-2.7 (m,1H), 2.7-3.0 (m,1H) 3.15 (m,1H), 3.35 (m,1H), 3.46 (s,3H), 7.22 (d,1H), 7.98 (d,1H), 8.10 (t,1H).

By the procedures described herein the following compounds of Tables 1 to 3 can be prepared. The compounds in Table 1, line 1 can be referred to as 1-1, 1-2, and 1-3 (as designated by line and column). All the other specific compounds covered in these Tables can be designated in an analogous fashion.

Table 1

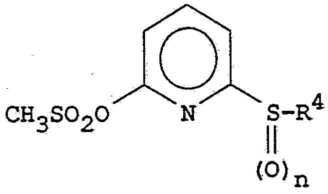


	R^3	Column No. 1	2	3
		n=		
1	$CH_2Si(Me)_3$	0	1	2
2	$CH_2CH_2Si(Me)_3$	0	1	2
3	$CH_2CH_2CH_2Si(Me)_3$	0	1	2
4	CH_2CN	0	1	2
5	CH_2CH_2CN	0	1	2
6	$CH_2CH_2CH_2CN$	0	1	2
7	$CH(Me)CN$	0	1	2
8	$CH_2CH(Me)CN$	0	1	2
9	$CH_2CH_2CH(Me)CN$	0	1	2
10	$CH_2CH(Me)CH_2CN$	0	1	2
11	CH_2OMe	0	1	2
12	CH_2CH_2OMe	0	1	2
13	$CH_2CH_2CH_2OMe$	0	1	2
14	$CH_2CH(Me)CH_2OMe$	0	1	2
15	CH_2SMe	0	1	2
16	CH_2CH_2SMe	0	1	2
17	CH_2CH_2SMe	0	1	2
18	$CH_2CH(Me)SMe$	0	1	2
19	CH_2SO_2Me	0	1	2
20	$CH_2CH_2SO_2Me$	0	1	2
21	$CH_2CH_2CH_2SO_2Me$	0	1	2
22	CH_2CH_2OAc	0	1	2
23	$CH_2CH_2CH_2OAc$	0	1	2
24	$CH_2CH(Me)OAc$	0	1	2
25	$CH_2CH_2OSO_2Me$	0	1	2
26	$CH_2CH_2CH_2OSO_2Me$	0	1	2
27	$CH_2CH(Me)OSO_2Me$	0	1	2
28	CH_2-cyclopropyl	0	1	2
29	CH_2CH_2-cyclopropyl	0	1	2
30	CH_2SCN	0	1	2
31	CH_2CH_2SCN	0	1	2
32	$CH_2CH_2CH_2SCN$	0	1	2
33	$CH_2CH_2NO_2$	0	1	2
34	$CH_2CH_2CH_2NO_2$	0	1	2
35	CH_2CO_2Me	0	1	2
36	$CH_2CH_2CO_2Me$	0	1	2
37	$CH(Me)CO_2Me$	0	1	2
38	$CH_2C(O)Me$	0	1	2
39	$CH_2CH_2C(O)Me$	0	1	2
40	$CH_2CH_2N(Me)_2$	0	1	2
41	$CH_2CH_2CH_2N(Me)_2$	0	1	2
42	$CH_2C{\equiv}CSi(Me)_3$	0	1	2
43	$CH_2C{\equiv}CCH_3$	0	1	2
44	$CH_2C{\equiv}CCH_2CH_3$	0	1	
45	$CH_2C(Cl)=CH_2$	0	1	
46	$CH_2CH=CCl_2$	0	1	
47	$CH_2CH=CHCl$	0	1	
48	$CH_2C(F)=CH_2$	0	1	

	$\underline{R}^3$	Column No.	
		1	2
		n=	
49	$CH_2CH=CF_2$	0	1
50	$CH_2C(F)=CF_2$	0	1
51	$CH_2CH_2C(F)=CF_2$	0	1
52	$CH_2CH_2CH=CF_2$	0	1
53	$CH_2CH_2C(F)=CH_2$	0	1
54	$CH_2CH_2C(Cl)=CCl_2$	0	1
55	$CH_2CH_2CH=CCl_2$	0	1
56	$CH_2CH_2C(Cl)=CH_2$	0	1
57	$CH_2CH_2CH=CFH$	0	1

	$\underline{R}^3$	Column No.		
		1	2	3
		n=		
58	$CH_2C\equiv CCH_2OMe$	0	1	2
59	$CH_2C\equiv CCH_2SMe$	0	1	2
60	$CH_2C(Me)_2CN$	0	1	2
61	$CH_2C(Me)_2OMe$	0	1	2
62	$CH_2C(Me)_2SMe$	0	1	2
63	CH_2CH_2OH	0	1	2
64	$CH_2CH(Me)OH$	0	1	2
65	$CH_2C(Me)_2OH$	0	1	2

Table 2



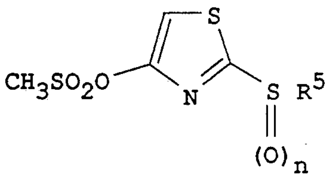
	$\underline{R}^4$	1	2	3
		n=		
66	$CH_2Si(Me)_3$	0	1	2
67	$CH_2CH_2Si(Me)_3$	0	1	2
68	$CH_2CH_2CH_2Si(Me)_3$	0	1	2
69	CH_2CN	0	1	2
70	CH_2CH_2CN	0	1	2
71	$CH_2CH_2CH_2CN$	0	1	2
72	$CH(Me)CN$	0	1	2
73	$CH_2CH(Me)CN$	0	1	2
74	$CH_2CH_2CH(Me)CN$	0	1	2
75	$CH_2CH(Me)CH_2CN$	0	1	2
76	CH_2SO_2Me	0	1	2
77	$CH_2CH_2SO_2Me$	0	1	2

	$\underline{R}^4$	1	2	3
		n=		
78	$CH_2CH_2CH_2SO_2Me$	0	1	2
79	CH_2CH_2OAc	0	1	2
80	$CH_2CH_2CH_2OAc$	0	1	2
81	$CH_2CH(Me)OAc$	0	1	2
82	$CH_2CH_2OSO_2Me$	0	1	2
83	$CH_2CH_2CH_2OSO_2Me$	0	1	2
84	$CH_2CH(Me)OSO_2Me$	0	1	2
85	$CH_2CH=CH-CN$	0	1	2
86	$CH_2CH=CH-CO_2CH_3$	0	1	2
87	CH_2SCN	0	1	2
88	CH_2CH_2SCN	0	1	2
89	$CH_2CH_2CH_2SCN$	0	1	2

		1	2	3
	$\underline{R}^4$	n=		
90	$CH_2CH_2NO_2$	0	1	2
91	$CH_2CH_2CH_2NO_2$	0	1	2
92	CH_2CO_2Me	0	1	2
93	$CH_2CH_2CO_2Me$	0	1	2
94	$CH(Me)CO_2Me$	0	1	2
95	$CH_2C(O)Me$	0	1	2
96	$CH_2CH_2C(O)Me$	0	1	2
97	$CH_2CH_2N(Me)_2$	0	1	2
98	$CH_2CH_2CH_2N(Me)_2$	0	1	2
99	$CH_2C(Cl){=}CH_2$	0	1	2
100	$CH_2CH{=}CCl_2$	0	1	2
101	$CH_2CH{=}CHCl$	0	1	2
102	$CH_2C(F){=}CH_2$	0	1	2
103	$CH_2CH{=}CF_2$	0	1	2
104	$CH_2C(F){=}CF_2$	0	1	2
105	$CH_2CH_2C(F){=}CF_2$	0	1	2

		1	2	3
	$\underline{R}^4$	n=		
106	$CH_2CH_2CH{=}CF_2$	0	1	2
107	$CH_2CH_2C(F){=}CH_2$	0	1	2
108	$CH_2CH_2C(Cl){=}CCl_2$	0	1	2
109	$CH_2CH_2CH{=}CCl_2$	0	1	2
110	$CH_2CH_2C(Cl){=}CH_2$	0	1	2
111	$CH_2CH_2CH{=}CFH$	0	1	2
112	$CH_2C{\equiv}CSi(Me)_3$	0	1	2
113	$CH_2C{\equiv}CCH_3$	0	1	2
114	$CH_2C{\equiv}CCH_2CH_3$	0	1	2
115	$CH_2C{\equiv}CCH_2OMe$	0	1	2
116	$CH_2C{\equiv}CCH_2SMe$	0	1	2
117	$CH_2C(Me)_2CN$	0	1	2
118	CH_2CH_2OH	0	1	2
119	$CH_2CH(Me)OH$	0	1	2
120	$CH_2C(Me)_2OH$	0	1	2

Table 3



		1	2	3
	$\underline{R}^3$	n=		
121	$CH_2Si(Me)_3$	0	1	2
122	$CH_2CH_2Si(Me)_3$	0	1	2
123	$CH_2CH_2CH_2Si(Me)_3$	0	1	2
124	CH_2CN	0	1	2
125	CH_2CH_2CN	0	1	2
126	$CH_2CH_2CH_2CN$	0	1	2

		1	2	3
	$\underline{R}^3$	n=		
127	$CH(Me)CN$	0	1	2
128	$CH_2CH(Me)CN$	0	1	2
129	$CH_2CH_2CH(Me)CN$	0	1	2
130	$CH_2CH(Me)CH_2CN$	0	1	2
131	CH_2SO_2Me	0	1	2
132	$CH_2CH_2SO_2Me$	0	1	2

		1	2	3
	R^3	n=		
133	$CH_2CH_2CH_2SO_2Me$	0	1	2
134	CH_2CH_2OAc	0	1	2
135	$CH_2CH_2CH_2OAc$	0	1	2
136	$CH_2CH(Me)OAc$	0	1	2
137	$CH_2CH_2OSO_2Me$	0	1	2
138	$CH_2CH_2CH_2OSO_2Me$	0	1	2
139	$CH_2CH(Me)OSO_2Me$	0	1	2
140	$CH_2CH{=}CH{-}CN$	0	1	2
141	$CH_2CH{=}CH{-}CO_2CH_3$	0	1	2
142	CH_2SCN	0	1	2
143	CH_2CH_2SCN	0	1	2
144	$CH_2CH_2CH_2SCN$	0	1	2
145	$CH_2CH_2NO_2$	0	1	2
146	$CH_2CH_2CH_2NO_2$	0	1	2
147	CH_2CO_2Me	0	1	2
148	$CH_2CH_2CO_2Me$	0	1	2
149	$CH(Me)CO_2Me$	0	1	2
150	$CH_2C(O)Me$	0	1	2
151	$CH_2CH_2C(O)Me$	0	1	2
152	$CH_2CH_2N(Me)_2$	0	1	2
153	$CH_2CH_2CH_2N(Me)_2$	0	1	2
154	$CH_2C(Cl){=}CH_2$	0	1	2
155	$CH_2CH{=}CCl_2$	0	1	2
156	$CH_2CH{=}CHCl$	0	1	2
157	$CH_2C(F){=}CH_2$	0	1	2
158	$CH_2CH{=}CF_2$	0	1	2
159	$CH_2C(F){=}CF_2$	0	1	2
160	$CH_2CH_2C(F){=}CF_2$	0	1	2
161	$CH_2CH_2CH{=}CF_2$	0	1	2
162	$CH_2CH_2C(F){=}CH_2$	0	1	2
163	$CH_2CH_2C(Cl){=}CCl_2$	0	1	2
164	$CH_2CH_2CH{=}CCl_2$	0	1	2
165	$CH_2CH_2C(Cl){=}CH_2$	0	1	2
166	$CH_2CH_2CH{=}CFH$	0	1	2
167	$CH_2C{\equiv}CSi(Me)_3$	0	1	2
168	$CH_2C{\equiv}CCH_3$	0	1	2
169	$CH_2C{\equiv}CCH_2CH_3$	0	1	2
170	$CH_2C{\equiv}CCH_2OMe$	0	1	2
171	$CH_2C{\equiv}CCH_2SMe$	0	1	2
172	$CH_2C(Me)_2CN$	0	1	2
173	CH_2CH_2OH	0	1	2
174	$CH_2CH(Me)OH$	0	1	2
175	$CH_2C(Me)_2OH$	0	1	2

Formulation/Utility

Compounds of this invention will generally be used in formulation with an agriculturally suitable carrier comprising a liquid or solid diluent or an organic solvent. Thus, the arthropodicidal compositions of the present invention comprise an effective amount of a compound of Formula I and at least one of (a) a surfactant, (b) an organic solvent, and (c) at least one solid or liquid diluent. Useful formulations include dusts, granules, baits, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like, consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up 100 weight percent.

	Weight Percent		
	Active Ingredient	Diluent	Surfactant
Wettable Powders	25-90	0-74	1-10
Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules, Baits and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents and solvents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ.

Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc.

Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer mill or fluid energy mill. Water-dispersible granules can be produced by agglomerating a fine powder composition; see for example, Cross et al., *Pesticide Formulations*, Washington, D.C., 1988, pp 251-259. Suspensions are prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-148, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pages 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can also be prepared as taught in DE 3,246,493.

For further information regarding the art of formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are worked up in conventional ways. Compound numbers refer to compounds in Index Table A.

Example A

Wettable Powder

Compound 1	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%.

Example B

Granule

Compound 1	10.0%
attapulgite granules (low volative matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%.

Example C

Extruded Pellet

Compound 1	25.0%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkylnaphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%.

Example D

Emulsifiable Concentrate

Compound 1	20.0%
blend of oil soluble sulfonates and polyoxyethylene ethers	10.0%
isophorone	70.0%.

The compounds of this invention exhibit activity against a wide spectrum of foliar-feeding, fruit-feeding, seed-feeding, aquatic and soil-inhabiting arthropods (term "arthropods" includes insects, mites and nematodes) which are pests of growing and stored agronomic crops, forestry, greenhouse crops, ornamentals, nursery crops, stored food and fiber products, livestock, household, and public and animal health. Those skilled in the art will appreciate that not all compounds are equally effective against all pests. Nevertheless, all of the compounds of this invention display activity against pests that include: eggs, larvae and adults of the Order Lepidoptera; eggs, foliar-feeding, fruit-feeding, root-feeding, seed-feeding larvae and adults of the Order Coleoptera; eggs, immatures and adults of the Orders Hemiptera and Homoptera; eggs, larvae, nymphs and adults of the Order Acari; eggs, immatures and adults of the Orders Thysanoptera, Orthoptera and Dermaptera; eggs, immatures and adults of the Order Diptera; and eggs, junveniles and adults of the Phylum Nematoda. The compounds of this invention are also active against pests of the Orders Hymenoptera, Isoptera, Siphonaptera, Blattaria, Thysanura and Pscoptera; pests belonging to the Class Arachnida and Phylum Platyhelminthes. The compounds are particularly active against southern corn rootworm (*Diabrotica undecimpunctata howardi*), aster leafhopper (*Mascrosteles fascifrons*), boll weevil (*Anthonomus grandis*), two-spotted spider mite (*Tetranychus urticae*), fall armyworm (*Spodoptera frugiperda*), black bean aphid (*Aphis fabae*), tobacco budworm (*Heliothis virescens*), rice water weevil (*Lissorhoptrus oryzophilus*), rice leaf beetle (*Oulema oryzae*), whitebacked planthopper (*Sogatella furcifera*), green leafhopper (*Nephotettix cincticeps*), brown planthopper (*Nilaparvata lugens*), small brown planthopper (*Laodelphax striatellus*), rice stem borer (*Chilo suppressalis*), rice leafroller (*Cnaphalocrocis medinalis*), black rice stink bug (*Scotinophara *lurida*), rice stink bug (*Lagynotomus elongatus*), rice bug (*Leptocorisa chinensis*), slender rice bug (*Cletus puntiger*), and southern green stink bug (*Nezara viridula*). See WO 90/10623 and WO 92/00673 for more detailed pest descriptions.

Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, semiochemicals, repellants, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of other agricultural protectants with which compounds of this invention can be formulated are: insecticides such as avermectic B, monocrotophos, carbofuran, tetrachlorvinphos, malathion, parathion-methyl, methomyl, chlordimeform, diazinon, deltamethrin, oxamyl, fenvalerate, esfenvalerate, permethrin, profenofos, sulprofos, triflumuron, diflubenzuron, methoprene, buprofezin, thiodicarb, acephate, azinphosmethyl, chlorpyrifos, dimethoate, fipronil, flufenprox, fonophos, isofenphos, methidathion, methamidophos, phosmet, phosphamidon, phosalone, pirimicarb, phorate, terbufos, trichlorfon, methoxychlor, bifenthrin, biphenate, cyfluthrin, fenpropathrin, fluvalinate, flucythrinate, tralomethrin, metaldehyde and rotenone; fungicides such as carbendazim, thiuram, dodine, maneb, chloroneb, benomyl, cymoxanil, fenpropidine, fenpropimorph, triadimefon, captan, thiophanate-methyl, thiabendazole, phosethyl-Al, chlorothalonil, dichloran, metalaxyl, captafol, iprodione, oxadixyl, vinclozolin, kasugamycin, myclobutanil, tebuconazole, difenoconazole, diniconazole, fluquinconazole, ipconazole, metconazole, penconazole, propiconazole, uniconzole, flutriafol, prochloraz, pyrifenox, fenarimol, triadimenol, diclobutrazol, copper oxychloride, furalaxyl, folpet, flusilazol, blasticidin S, diclomezine, edifenphos, isoprothiolane, iprobenfos, mepronil, neo-asozin, pencycuron, probenazole, pyroquilon, tricyclazole, validamycin, and flutolanil; nematocides such as aldoxycarb, fenamiphos and fosthietan; bactericides such as oxytetracyline, streptomycin and tribasic copper sulfate; acaricides such as binapacryl, oxythioquinox, chlorobenzilate, dicofol, dienochlor, cyhexatin, hexythiazox, amitraz, propargite, tebufenpyrad and fenbutatin oxide; and biological agents such as Bacillus thuringiensis and baculovirus.

In certain instances, combinations with other arthropodicides having a similiar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

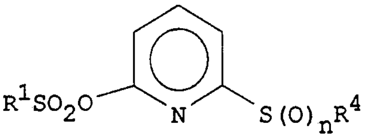
Arthropod pests are controlled and protection of agronomic crops, animal and human health is achieved by applying one or more of the compounds of this invention, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. Thus, the present invention further comprises a method for the control of foliar and soil inhabiting arthropods and nematode pests and protection of agronomic and/or nonagronomic crops, comprising applying one or more of the compounds of Formula I, or compositions containing at least one such compound, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. A preferred method of application is by spraying. Alternatively, granular formulations of these compounds can be applied to the plant foliage or the soil. Other methods of application include direct and residual sprays, aerial sprays, seed coats, systemic uptake, baits, eartags, boluses, foggers, fumigants, aerosols, and many others. The compounds can be incorporated into baits that are consumed by the arthropods or in devices such as traps and the like.

The compounds of this invention can be applied in their pure state, but most often application will be of a formulation comprising one or more compounds with suitable carriers, diluents, and surfactants and possibly in combination with a food depending on the contemplated end use. A preferred method of application involves spraying a water dispersion or refined oil solution of the compounds. Combinations with spray oils, spray oil concentrations, spreader stickers, adjuvants, and synergists and other solvents such as piperonyl butoxide often enhance compound efficacy.

The rate of application required for effective control will depend on such factors as the species of arthropod to be controlled, the pest's life cycle, life stage, its size, location, time of year, host crop or animal, feeding behavior, mating behavior, ambient moisture, temperature, and the like. Under normal circumstances, application rates of about 0.01 to 2 kg of active ingredient per hectare are sufficient to control pests in agronomic ecosystems, but as little as 0.001 kg/hectare may be sufficient or as much as 8 kg hectare may be required. For nonagronomic applications, effective use rates will range from about 1.0 to 50 mg/square meter but as little as 0.1 mg/square meter may be sufficient or as much as 150 mg/square meter may be required.

The following TESTS demonstrate the control efficacy of compounds of this invention on specific pests. The pest control protection afforded by the compounds is not limited, however, to these species. See Index Tables A, B and C for compound descriptions.

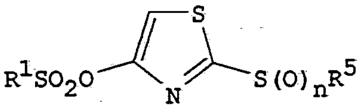
Index Table A



CMPD	R^1	R^4	n	Physical Properties (mp°C)
1	Me	$CH_2Si(Me)_3$	0	59-61
2	Me	$CH_2CH_2C(F)=CF_2$	0	48-52
3	Me	CH_2CO_2Et	0	oil
4	Me	$CH_2CH_2CH_2CN$	0	80-84
5	Me	$CH_2CH_2C(F)=CF_2$	2	oil
6	Me	$CH_2CH_2C(F)=CF_2$	1	oil
7	Me	$CH_2C(Cl)=CH_2$	0	oil
8	Me	CH_2CH_2CN	0	oil
9	Me	$CH_2(Me)C(O)Me$	0	oil
10	Me	$CH_2C(O)Me$	0	oil
11	Me	$CH_2CH_2CH_2CN$	1	oil
12	Me	$CH_2CH_2CH_2CN$	2	oil
13	Me	CH_2CH_2CN	1	75-78
14	Me	CH_2CH_2CN	2	oil
15	Me	$CH_2Si(Me)_3$	1	oil
16	Me	$CH_2Si(Me)_3$	2	85-87
17	Me	$CH_2CH_2C{\equiv}CH$	0	oil
18	Me	$CH_2CH_2C(Br)=CH_2$	0	oil
19	Me	$CH_2CH_2CH_2C{\equiv}CH$	0	oil
20	Me	$CH_2CH_2C(Br)=CH_2$	1	82-89
21	Me	$CH_2CH_2C(Br)=CH_2$	2	oil
22	Me	$CH_2CH_2CH_2C{\equiv}CH$	1	oil
23	Me	$CH_2CH_2CH_2C{\equiv}CH$	2	oil
24	Me	$CH_2CH_2CH(CN)CH_3$	0	oil
25	$ClCH_2$	$CH_2CH_2CH_2CN$	0	oil
26	Et	$CH_2CH_2CH_2CN$	0	oil
27	$ClCH_2$	CH_2CH_2CN	0	oil

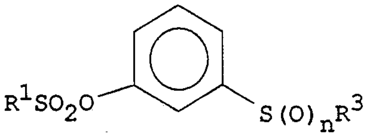
CMPD	R^1	R^4	n	Physical Properties (mp°C)
28	Et	CH_2CH_2CN	0	oil
29	Et	$CH_2Si(Me)_3$	0	oil
30	$ClCH_2$	$CH_2CH_2C(F)=CF_2$	0	oil
31	Et	$CH_2CH_2C(F)=CF_2$	0	oil
32	$ClCH_2$	$CH_2CH_2C(F)=CF_2$	2	oil
33	Et	$CH_2CH_2C(F)=CF_2$	2	oil
34	$ClCH_2$	$CH_2CH_2CH_2CN$	1	oil
35	$ClCH_2$	$CH_2CH_2CH_2CN$	2	oil
36	Et	$CH_2CH_2CH_2CN$	1	oil
37	Et	$CH_2CH_2CH_2CN$	2	oil
38	$ClCH_2$	$CH_2CH_2CH_2CN$	1	oil
39	$ClCH_2$	$CH_2CH_2CH_2CN$	2	oil
40	Et	$CH_2CH_2CH_2CN$	1	oil
41	Et	$CH_2CH_2CH_2CN$	2	oil
42	Me	$CH_2C(O)NMe_2$	0	oil
43	Me	$CH_2C(O)NH$-i-Pr	0	80-85

Index Table B



CMPD	R^1	R^5	n	Physical Properties (mp°C)
44	Me	$CH_2Si(Me)_3$	0	64-66
45	Me	$CH_2CH_2C(F)=CF_2$	0	oil
46	Me	$CH_2C(Me)=CH_2$	0	oil
47	Me	$CH_2Si(Me)_3$	1	oil
48	Me	$CH_2C(Me)=CH_2$	1	oil
49	$ClCH_2$	$CH_2Si(Me)_3$	0	oil
50	Et	$CH_2Si(Me)_3$	0	oil
51	$ClCH_2$	$CH_2CH_2C(F)=CF_2$	0	oil
52	Et	$CH_2CH_2C(F)=CF_2$	0	oil

Index Table C



CMPD	R^1	R^3	n	Physical Properties (mp°C)
53	Me	$CH_2CH_2C(F){=}CF_2$	0	oil
54	Me	$CH_2Si(Me)_3$	0	oil
55	Me	$CH_2CH_2C(F){=}CF_2$	1	oil
56	Me	$CH_2Si(Me)_3$	1	oil

TEST A

Southern Corn Rootworm

The units, each consisting of an 8-ounce (230 mL) plastic cup containing a one-inch square of a soybean-wheat germ diet were prepared. Solutions of each of the test compounds (acetone/distilled water 75/25) were sprayed into the cup. Spraying was accomplished by passing the cup, on a conveyor belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.5 pounds active ingredient per acre (about 0.55 kg/ha) at 30 psi (207 kPa). After the spray on the cups had dried, five second-instar larvae of the southern corn rootworm (*Diabrotica undecimpunctata howardi*) were placed into each cup. The cups were then covered and held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 1, 2, 4, 6, 7, 8, 9, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 46, 47, 50, 51, 53, 54, 56.

TEST B

Aster Leafhopper

Test units were prepared from a series of 12-ounce (350 mL) cups, each containing oat (*Avena sativa*) seedlings in a 1-inch (2.5 cm) layer of sterilized soil and a 1/2-inch layer of sand. The test units were sprayed as described in Test A with individual solutions of spraying, between 10 and 15 adult aster leafhoppers (*Macrosteles fascifrons*) were aspirated into each of the cups covered with vented lids. The cups were held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 1, 2, 4, 5, 6, 7, 8, 11, 12, 13, 17, 18, 19, 20, 21, 22, 24, 25, 26, 27, 28, 29, 30, 31, 33, 46, 51, 52, 53, 55.

TEST C

Boll Weevil

Five adult boll weevils (*Anthonomus grandis grandis*) were placed into each of a series of 9-ounce (260 mL) cups. The test units were sprayed as described in Test A with individual solutions of the below-listed compounds. Each cup was then covered with a vented lid and held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 2, 6, 8, 12, 17, 19, 46.

TEST D

Black Bean Aphid

Individual nasturtium leaves were infested with 10 to 15 aphids (all stages of *Aphis fabae*) and sprayed with their undersides facing up as described in Test A. The leaves were then set in 3/8 inch diameter vials containing 4 ml of sugar water solution and covered with a clear plastic 1-ounce portion cup to prevent escape of aphids that drop from the leaves. The test units were held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 1, 2, 4, 6, 8, 13, 14, 15, 16, 17, 19, 23, 25, 27, 28, 30.

TEST E

Two-Spotted Spider Mites

The test procedure for Test D was used for efficacy against adult two-spotted spider mites (*Tetranychus urticae*), except that pre-infested one inch square kidney leaves were sprayed and then placed on 4 inch plastic lid with 4 inch wet cotton square was used. Test E is read at 48 hours for mortality. Of the compounds tested, the following gave mortality level of 80% or higher: 1, 2, 4, 11, 12, 14, 17, 18, 19, 23, 27, 29, 30, 31, 49, 50.

TEST F

Contact Activity Against Green Leafhopper Nymphs

Three rice (*Oryza sativa*) seedlings, 1.5 leaf stage and about 10 cm tall were transplanted into a 1/2 ounce (14 mL) plastic cup containing Kumiai Brown artificial soil. Seven milliliters of distilled water was then added to the cup. The test chemical was prepared by first dissolving the chemical in acetone and then adding water to produce a final test concentration of 75:25 (acetone:water). Four plastic cups, each cup serving as a replicate, were then placed on a spray chamber turntable. The cups were sprayed for 45 seconds with 50 mL of the chemical solution at a pressure of 2.0 kg/cm^2 with air atomizing spray nozzles. The turntable completes 7.5 rotations during the 45 second spray interval.

After chemical application, the treated cups were held in a vented enclosure to dry for about 2 h. After drying, the cups were placed into conical shaped test units and the surface of the soil covered with 2 to 3 mm of quartz sand. Eight to ten 3rd-instar nymphs of the green leafhopper (*Nephotettix cincticeps*) were transferred into the test units using an aspirator. The test units were held at 27°C and 65% relative humidity. Counts of the number of live and dead nymphs were taken at 24 and 48 h post-infestation. Insects which cannot walk are classified as dead. Of the compounds tested, the following gave mortality levels of 80% or higher at 48 h at 100 ppm: 1, 2, 4, 7, 11, 17, 18, 19, 20, 21, 23, 24, 53, 55.

TEST G

Contact Activity Against Brown Planthopper Nymphs

Three rice (*Oryza sativa*) seedlings, 1.5 leaf stage and about 10 cm tall were transplanted into a 1/2 oz. (14 mL) plastic cup containing Kumiai Brown artificial soil. Seven milliliters of distilled water was then added to the cup. The test chemical was prepared by first dissolving the chemical in acetone and then adding water to produce a final test concentration of 75:25 (acetone:water). Four plastic cups, each cup serving as a replicate, were then placed on a spray chamber turntable. The cups were sprayed for 45 seconds with 50 mL of the chemical solution at a pressure of 2.0 kg/cm^2 with air atomizing spray nozzles. The turntable completes 7.5 rotations during the 45 second spray interval. After chemical application, treated cups were held in a vented enclosure to dry for about 2 h. After drying, the cups were placed into conical shaped test units and the surface of the soil covered with 2 to 3 mm of quartz sand. Eight to ten 3rd-instar nymphs of the brown planthopper (*Nilaparvata lugens*) were then transferred into the test units using an aspirator. The test units were held at 27°C and 65% relative humidity. Counts of the number of live and dead nymphs are taken at 24 and 48 h post-infestation. Insects which cannot walk are classified as dead. Of the compounds tested, the following gave mortality levels of 80% or higher at 48 h at 100 ppm: 1, 2, 4, 7, 11, 17, 18, 19, 20, 23, 24, 46, 53, 55.

TEST H

Solution Systemic Activity Against Green Leafhopper Nymphs

The test chemical was added directly into 10 mL of distilled water and dissolved completely. This chemical solution was poured into a conical shaped test unit. Three rice seedlings were then positioned in the unit by a notched sponge disk. The sponge disk allows complete immersion of the seedling root systems in the chemical solution, while the aerial portion of the plant is isolated above the solution. The sponge also prevents the test nymphs from accidentally contacting the test solution. A 7 to 10 mm space, between the surface of the chemical solution and the bottom of the sponge disk, prevents accidental chemical contamination of the sponge. The rice seedlings were allowed to absorb the chemical from the solution for 24 h in a growth chamber held at 27°C and 65% relative humidity. Eight to ten 3rd-instar nymphs of the green leafhopper (*Nephotettix cincticeps*) were then transferred into the test units using an aspirator. The infested units were held under the same temperature and humidity conditions described above. Counts of the number of live and dead nymphs were taken at 24 and 48 h post-infestation. Inspects which cannot walk are classified as dead. Of the compounds tested, the following gave mortality levels of 80% or higher at 48 h at 100 ppm: 17,19,55.

TEST I

Solution Systemic Activity Against Brown Planthopper Nymphs

The test chemical was added directly into 10 mL of distilled water and dissolved completely. This chemical solution was poured into a conical shaped test unit. Three rice seedlings were then positioned in the unit by a notched sponge disk. The sponge disk allows complete immersion of the seedling root systems in the chemical solution, while the aerial portion of the plant is isolated above the solution. The sponge also prevents the test nymphs from accidentally contacting the test solution. A 7 to 10 mm space, between the surface of the chemical solution and the bottom of the sponge disk, prevents accidental chemical contamination of the sponge. The rice seedlings were allowed to absorb the chemical from the solution for 24 h in a growth chamber held at 27°C and 65% relative humidity. Eight to ten 3rd-instar nymphs of the brown planthopper (*Nilaparvata lugens*) were then transferred into the test units using an aspirator. The infested units were held under the same temperature and humidity conditions described above. Counts of the number of live and dead nymphs are taken at 24 and 48 h post-infestation. Inspects which cannot walk are classified as dead. Of the compounds tested, the following gave mortality levels of 80% or higher at 48 h at 100 ppm: 17, 18, 19, 55.

CLAIMS

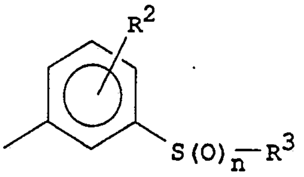
1. A compound of the formula

$$R^1 - SO_2 - O - Q$$

I

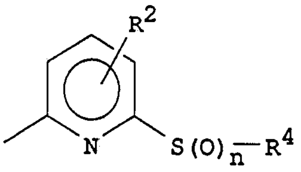
wherein:

Q is selected from the group



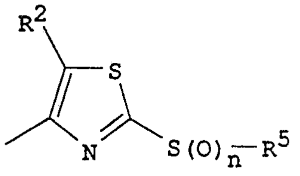
Q-1

,



Q-2

and



Q-3

;

R^1 is selected from the group C_1-C_3 alkyl and C_1-C_3 haloalkyl;

R^2 is selected from the group H, C_1-C_2 alkyl, C_1-C_2 haloalkyl, C_1-C_2 alkoxy, C_1-C_2 haloalkoxy, C_1-C_2 alkylthio, C_1-C_2 haloalkylthio, C_1-C_2 alkylsulfinyl, C_1-C_2 haloalkylsulfinyl, C_1-C_2 alkylsulfonyl, C_1-C_2 haloalkylsulfonyl, amino, C_1-C_2 alkylamino, C_2-C_4 dialkylamino, C_2-C_3 alkoxycarbonyl; phenyl optionally substituted with halogen, CN or NO_2; halogen; NO_2; and CN;

R^3 is selected from the group C_1-C_6 alkyl substituted with R^6, C_3-C_6 alkenyl substituted with R^6, C_3-C_6 alkynyl substituted with R^7 and C_4-C_7 cycloalkylalkyl optionally substituted with R^8; wherein when R^3 is C_3-C_6 alkenyl substituted with R^7 and R^7 is 1 to 3 halogens, then n is 0 or 1;

R^4 and R^5 are independently selected from the group C_1-C_6 alkyl substituted with R^9, C_2-C_6 alkenyl substituted with R^{10}, and C_2-C_6 alkynyl substituted with R^{10};

R^6 is selected from the group CN, SCN, NO_2, OH, OR^{11}, SR^{11}, $S(O)R^{11}$, SO_2R^{11}, $OC(O)R^{11}$, OSO_2R^{11}, $Si(R^{11})(R^{12})(R^{13})$, CO_2R^{11}, $C(O)N(R^{11})R^{12}$, $C(O)R^{11}$ and $N(R^{11})R^{12}$;

R^7 is selected from the group 1-3 halogens, C_1-C_3 alkyl, CN, SCN, NO_2, OH, OR^{11}, SR^{11}, $S(O)R^{11}$, SO_2R^{11}, $OC(O)R^{11}$, OSO_2R^{11}, $Si(R^{11})(R^{12})(R^{13})$, CO_2R^{11}, $C(O)N(R^{11})R^{12}$, $C(O)R^{11}$ and $N(R^{11})R^{12}$;

R^8 is selected from the group 1-3 halogens, CN and C_1-C_2 alkyl;

R^9 is selected from the group CN, SCN, NO_2, OH, OR^{14}, SR^{14}, $S(O)R^{11}$, SO_2R^{11}, $OC(O)R^{11}$, OSO_2R^{11}, $Si(R^{11})(R^{12})(R^{13})$, CO_2R^{11}, $C(O)N(R^{11})R^{12}$, $C(O)R^{11}$ and $N(R^{11})R^{12}$;

R^{10} is selected from the group 1-3 halogens, C_1-C_3 alkyl, CN, SCN, NO_2, OH, OR^{11}, SR^{11}, $S(O)R^{11}$, SO_2R^{11}, $OC(O)R^{11}$, OSO_2R^{11}, $Si(R^{11})(R^{12})(R^{13})$, CO_2R^{11}, $C(O)N(R^{11})R^{12}$, $C(O)R^{11}$ and $N(R^{11})R^{12}$;

R^{11}, R^{12} and R^{13} are independently selected from the group C_1-C_3 alkyl and C_1-C_3 haloalkyl;

R^{14} is selected from C_1-C_3 haloalkyl; and

n is 0, 1 or 2.

2. A compound according to Claim 1 wherein:

R^1 is CH_3;
R^2 is selected from the group H, CH_3, halogen, CF_3 and CN;
R^6 is selected from the group CN, SCN, $Si(R^{11})(R^{12})(R^{13})$, OR^{11} and SR^{11};
R^7 is selected from the group 1-3 halogens, CN, SCN, $Si(R^{11})(R^{12})(R^{13})$, OR^{11} and SR^{11};
R^9 is selected from the group CN, SCN, $Si(R^{11})(R^{12})(R^{13})$, OR^{14} and SR^{14}; and
R^{10} is selected from the group 1-3 halogens, CN, SCN, $Si(R^{11})(R^{12})(R^{13})$, OR^{11} and SR^{11}.

3. A compound according to Claim 2 wherein Q is Q-1.

4. A compound according to Claim 2 wherein Q is Q-2.

5. A compound according to Claim 2 wherein Q is Q-3.

6. An arthropodicidal composition comprising an effective amount of a compound according to any one of Claims 1 to 5 and a carrier therefor.

7. A method for controlling arthropods comprising applying to the arthropods or to their environment an effective ammount of a compound according to any one of Claims 1 to 5.