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Bellina

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[54] **N-ALKOXY-N-ALKYLAMINO SUBSTITUTED DITHIAZOLIUM SALTS**

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[52] **U.S. Cl.** ..... **260/306.8 R;** 424/270

[51] **Int. Cl.** **C07d 91/70**

[58] **Field of Search** ..... 260/306.8 R

[56] **References Cited**

UNITED STATES PATENTS

3,166,564 1/1965 Diveley ..... 260/306.8 R

Primary Examiner—R. Gallagher

[57] **ABSTRACT**

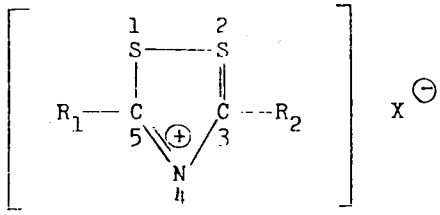
Novel 3,5-bis(N-alkoxy-N-alkylamino)-1,2,4-dithiazolium salts and 3-dialkylamino-5-(N-alkoxy-N-alkylamino)-1,2,4-dithiazolium salts useful as insecticides, miticides, and fungicides.

3 Claims, No Drawings

N-ALKOXY-N-ALKYLAMINO SUBSTITUTED DITHIAZOLIUM SALTS

BACKGROUND OF THE INVENTION

U.S. Pat. No. 3,166,564 issued Jan. 19, 1965, discloses 3,5-bis(substituted amino)-1,2,4-dithiazolium salts of the formula



wherein

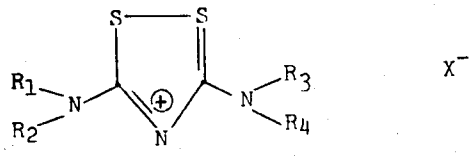
X represents an anion of an acid having an ionization constant of at least 1×10^{-7}, and R_1 and R_2 represent certain substituted secondary amino groups. Examples given for R_1 and R_2 include dimethylamino, diethylamino, dipropylamino, dibutylamino, dilaurylamino, didodecylamino, dicyclohexylamino, methylstearylamino, distearylamino, diphenylamino, ditolylamino, tolylphenylamino, dinaphthylamino, methylphenylamino, butyltolylamino, cyclohexylphenylamino, piperidino and morpholino. The compounds are said to be useful to defoliate plants, specifically cotton.

Some of the compounds disclosed in U.S. Pat. No. 3,166,564 are also known in the art as housefly chemosterilants [J. Econ. Ent. 62 (1969), 522, J. Med. Chem. 15 (1972) 315, and J. Econ. Ent. 65, (1972) 390] and one of them, 3,5-bis(diethylamino)- 1,2,4-dithiazolium chloride, is known as a Japanese beetle chemosterilant [J. Econ. Ent. 63 (1970) 458].

It has also been discovered that compounds of U.S. Pat. No. 3,166,564 are miticides, insecticides, and fungicides. U.S. application Ser. No. 298,485, filed Oct. 18, 1972, as a continuation-in-part of U.S. application Ser. No. 149,328, filed June 2, 1971 discloses the use of the compounds as miticides and insecticides. U.S. application Ser. No. 298,486, filed Oct. 18, 1972, discloses the use of the compounds as fungicides. The three applications noted are now abandoned.

SUMMARY OF THE INVENTION

In one embodiment, this invention is a class of novel insecticidal, miticidal, and fungicidal N-alkoxy-N-alkylamino substituted dithiazolium salts which can be represented by formula I



where

R_1 and R_3 are C_1–C_2 alkyl;

R_2 is C_1–C_2 alkyl or C_1–C_2 alkoxyl;

R_4 is C_1–C_2 alkoxyl; and

X^- is an anion of the corresponding acid HX having an ionization constant of at least 1×10^{-7}.

Preferred because of highest activity are those compounds of formula I where

R_1, R_2 and R_3 are C_1–C_2 alkyls; and

R_4 is C_1–C_2 alkoxyl.

In another embodiment, this invention is a method for protecting plants from mites, fungi, aphids, Colorado potato peel, and Mexican bean bettle by applying to the plant foliage a mitidically, fungicidally, and insecticidally effective amount, but less than a defoliating amount, of at least one compound of formula I.

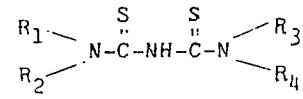
In another embodiment, this invention is a method of controlling mosquitoes, which comprises applying to mosquito larvae an insecticidally effective amount of at least compound of formula I.

In formula I, X^- is an anion of any acid HX with an ionization constant of at least 1×10^{-7}. Examples of such acids are HCl, HBr, HF, HI, H_2SO_4, HSCN, H_3PO_4, H_2SO_3, acetic acid, oxalic acid, tartaric acid, benzoic acid, and N-lauryl-N-methyl-2-aminoethanesulfonic acid. The miticidal, fungicidal, and insecticidal activity of the salts of formula I is attributable to the cation.

DETAILED DESCRIPTION OF THE INVENTION

Synthesis on the Compound

The compounds of formula I can be made by oxidation of an appropriate 1,1,5,5-tetrasubstituted dithiobiuret of formula II in the presence of an acid HX.



II

The reaction can be carried out under the general conditions described in U.S. Pat. No. 3,166,564 for oxidation of 1,1,5,5-tetrasubstituted dithiobiurets in the presence of acid to produce 3,5-bis(substituted amino)-1,2,4-dithiazolium salts. As taught by the same reference, one salt can be converted to a salt of another acid by simple displacement or by reacting one salt with the metal salt of another acid.

The 1,1,5,5-tetrasubstituted dithiobiurets of formula II can be prepared as also described in U.S. Pat. No. 3,166,564 by reacting an appropriate substituted thiocarbamoly chloride with an alkali metal or ammonium thiocyanate to form a corresponding substituted thiocarbamoly isothiocyanate, then reacting the latter with an appropriate secondary amine. The appropriate secondary amines for use in preparing the compounds of formula I of this invention are the following:

N,O-dimethylhydroxylamine

N,O-diethylhydroxylamine

N-ethyl-O-methylhydroxylamine

O-ethyl-N-methylhydroxylamine

For preparing the compounds of formula I wherein R_2 is C_1–C_2 alkyl, the appropriate thiocarbamoly chlorides are:

dimethylthiocarbamoyl chloride

diethylthiocarbamoyl chloride
ethylmethylthiocarbamoyl chloride.

For preparing the compounds wherein R_2 is C_1–C_2 alkoxyl, the appropriate thiocarbamoyl chlorides are:

N-methoxy-N-methylthiocarbamoyl chloride
N-ethyl-N-methoxythiocarbamoyl chloride
N-ethoxy-N-methythiocarbamoyl chloride
N-ethoxy-N-ethylthiocarbamoyl chloride.

The foregoing alkoxy substituted thiocarbamoyl chlorides can be prepared by reacting the above disubstituted hydroxyl amines with thiophosgene.

Formulation and Use of the Compounds

Miticidal, fungicidal, and insecticidal compositions can be prepared by mixing at least one compound of formula I with an inert carrier and/or a surface-active agent to provide watersoluble powders, dusts, and liquid concentrates. The inert carrier can be a finely divided solid, water, or an organic liquid. The surface-active agent can be any anionic, cationic, or non-ionic agent which has heretofore been generally employed in pest-control compositions or an equivalent. Suitable surfaceactive agents are set forth for example in "Detergents and Emulsifiers 1970 Annual" by John W. McCutcheon, Inc.

Water-soluble powders of this invention contain at least one compound of formula I together with an inert, solid carrier which may itself be either water-soluble or water-insoluble. One or more surface-active agents may also be present to improve speed of wetting, dispersion, and solution in water.

The most suitable water-insoluble carriers are synthetic silicas, magnesium silicate, and natural clays, such as, diatomaceous earth, kaolinites, attapulgite clay and the like. Water-soluble carriers include sugar, calcium sulfite dihydrate, sodium sulfite, urea, and the like.

The water-soluble powder formulations contain from about 25 to 99% by weight of at least one compound of formula I and 1 to 75% by weight of inert carrier. Preferably, they also contain about 0.1% to 10% of weight of surface-active agents replacing equivalent amounts of inert carrier.

The more dilute of these water-soluble powders can also be used as dusts, and more concentrated compositions can be diluted with conventional dust diluents, such as to a range of 1 to 25% active ingredient.

Liquid concentrates of the invention contain at least one compound of formula I together with a solvent consisting of water or an organic liquid or any suitable mixture of these. Organic liquids which can be used include dimethylformamide, ethylene glycol, diethylene glycol, propylene glycol, the monomethyl or ethyl ethers of the preceding glycols, methanol, ethanol, propanol, acetone, and other ketones.

Liquid concentrates of the invention contain from about 10 to about 60% by weight of active ingredient (at least one compound of formula I), with the remainder comprising the solvents listed above either individually or in admixture.

These liquid compositions can be diluted with water and applied in the conventional manner to plants, but they are also particularly suitable for application at high concentration in the typical ultra-low-volume or low-volume application from aircraft or ground sprayer. The water-soluble powders can also be dissolved or dispersed in appropriate liquid carriers and applied as low-volume sprays.

Compositions of this invention can contain in addition to at least one compound of formula I conventional insecticides, miticides, bactericides, and fungicides or other agricultural chemicals such as fruit sap agents, fruit thinning compounds, fertilizer ingredients, and the like.

Many species of mites which cause damage to fruits, field crops, vegetables, ornamentals, animals, birds and man are controlled by the compounds of this invention. The following is a list of representative susceptible mites along with the types of damage that they can cause: *Panonychus ulmi* (European red mite) and *Tetranychus utricae* (two spotted mite) which are commonly called "orchard mites," and which attack a great many deciduous trees, such as apple, pear, cherry, plum and peach trees; *Tetranychus atlanticus* (Atlantic or strawberry mite), *T. cinnabarinus* (carmine spider mite) and *T. pacificus* (Pacific mite); which attack cotton and numerous other crop plants; *Paratetranychus citri* (citrus red mite) and others which attack citrus; *Phyllocoptruta oleivora* which causes citrus rust; *Bryobia practiosa* (clover mite) which attacks clover, alfalfa and other crops; *Aceria neocynodomis* which attacks grasses and other plants; *Tyrophagus lintneri* which is a serious pest in stored foods and on cultivated mushrooms; *Lepidoglyphus destructor* which injures Kentucky bluegrass seed in storage, and *Dermanyssus gallinae* (poultry mite) which reduce egg production and increase mortality of young chicks.

The compounds of formula I are also useful for control of certain insect species such as: the apple aphid, *Aphis pomi;* bean aphid, *Aphis fabae;* green peach aphid, *Myzus persicae;* pea aphid, *Macrosiphum pisi;* potato aphid, *Macrosiphum euphobiae;* Colorado potato beetle, *Leptinotarsa decemlineata;* Mexican bean beetle, *Epilacbna varivestis;* Southern armyworm, *Prodenia eridania;* bollworms, *Heliothis zea* and *Heliothis virescens;* mosquitoes, *Aedes* spp., *Anopheles* spp., and *Culex* spp.,; and boll weevils, *Anthonomus grandis.*

The compounds of formula I are called fungicides, although in the strictest sense they do not necessarily kill fungi; they have an anti-sporulant effect on fungi, and control many plant diseases, including the tomato late blight pathogen, *Phytophthora infestans*, the cucumber powdery mildew pathogen, *Erysiphe cichoracearum*, the apple scab pathogen, *Venturia inaequalis*, and the downy mildew pathogen, *Pseudoperonospora cubensis.*

The compounds of formula I can be used for the protection of plants such as fruit-bearing trees, nut-bearing trees, ornamental trees, forest trees, vetetable crops, horticultural crops (including ornamental, small fruit and berries), and grain and seed crops. They are especially suited to protect apple, citrus, and peach trees, cotton, potatoes, peas, corn, and beans from mites, fungi, and certain insects.

Rates for application of the compounds of formula I to field crops are from 0.01 to 4 kilograms of active ingredient per hectare. For the more active compounds, including the preferred compounds, rates in the range of 0.01 to 0.8 kg/ha. are preferred. The compounds should be applied to ornamental, nut, and fruit trees by spraying to run-off with a solution of suspension containing about 10 to 8,000 ppm, preferably about 10 to 4,000 ppm of active ingredient. The compounds, of

course, vary in their pesticidal activity and phytotoxicity. The compounds must be used in an amount which is effective to control the pests but less than the amount which will cause defoliation or other severe symptoms of phytotoxicity. The optimum amount for a given compound depends upon a number of variables which are well known to those skilled in the art of plant protection. These include, but are not limited to, the species of mite, fungus, or insect to be controlled, weather conditions expected, type of crop, stage of development of the crop and the interval between applications. It may be necessary or desirable to repeat application within the ranges given one or more times at intervals of 1 to 60 days.

The compounds of formula I may be used for control of mosquito larvae breeding in swampy and other moist locations. The quantity of chemicals used depends on the amount of water present in the area and on the percent control of the larvae desired. Greater amounts of water present and a desired high percent kill require correspondingly greater amounts of active ingredient. In general marshy areas where the water does not exceed one foot in depth may require 0.1 to 3 kg of active ingredient per hectare. The amount actually used should be predetermined from a knowledge of the area to be treated.

EXAMPLE 1

Preparation of 3-Dimethylamino-5-(N-methoxy-N-methylamino)-1,2,4-dithiazolium bromide

To a solution of 14.6 parts of dimethylthiocarbamoyl isothiocyanate in 100 parts of acetone at room temperature is added dropwise over a 15-minute period 6.1 parts of methoxymethylamine, followed by the dropwise addition of 17 parts of 48% aqueous hydrobromic acid over 15 minutes. To this solution was added dropwise over a 30-minute period 11.35 parts of 30% hydrogen peroxide. The reaction was then concentrated under reduced pressure at 50°C., cooled to room temperature and diluted with a 1:1 solution of acetone:ethyl acetate. The product which precipitated as an oil was washed several times with acetone and finally crystallized upon scratching under acetone. It was recrystallized from ethanol to furnish 3.2 parts of the product, m.p. 143°–144°C.dec. Another recrystallization from acetonitrile provided purer product, m.p. 150.5°–151°C. dec. Finally, the product was dissolved in water, treated with darco, filtered and the water evaporated to afford the purified desired material, m.p. 151.5°–152.5°C. dec.

By replacing at least one of the above reagents with the appropriate thiocarbamoyl isothiocyanate, disubstituted amine and/or acid the following compounds can be similarly prepared:

3-dimethylamino-5-(N-ethoxy-N-methylamino)-1,2,4-dithiazolium chloride
3-dimethylamino-5-(N-ethoxy-N-ethylamino)-1,2,4-dithiazolium iodide
3-dimethylamino-5-ethylmethoxyamine-1,2,4-dithiazolium fluoride
3-diethylamino-5-(N-ethoxy-N-methylamino)-1,2,4-dithiazolium tartarate
3-diethylamino-5-(N-ethoxy-N-ethylamino)-1,2,4-dithiazolium oxalate
3-diethylamino-5-ethylmethoxyamino-1,2,4-dithiazolium bromide
3-diethylamino-5-(N-methoxy-N-methylamino)-1,2,4-dithiazolium bisulfite
3-(N-ethoxy-N-methylamino)-5-ethylmethylamino-1,2,4-dithiazolium thiocyanate
3-(N-ethoxy-N-ethylamino)-5-ethylmethylamino-1,2,4-dithiazolium benzoate
3-ethylmethoxyamino-5-ethylmethylamino-1,2,4-dithiazolium dihydrogen phosphate
3-ethylmethylamino-5-(N-methoxy-N-methylamino)-1,2,4-dithiazolium bisulfate
3-ethoxymethylamino-5-(N-methoxy-N-methylamino)-1,2,4-dithiazolium acetate
3-ethoxyethylamino-5-(N-methoxy-N-methylamino)-1,2,4-dithiazolium bisulfate
3,5-bis(N-methoxy-N-methylamino)-1,2,4-dithiazolium chloride
3,5-bis(N-ethoxy-N-ethylamino)-1,2,4-dithiazolium acetate
3,5-bis(ethylmethoxyamino)-1,2,4-dithiazolium iodide
3,5-bis(N-ethoxy-N-methylamino)-1,2,4-dithiazolium 4-laruyl-N-methyl-2-aminoethane sulfonate

EXAMPLE 2

	Percent
Product of Example 1	25.0
Water	25.0
Ethylene glycol	40.0
Ethanol	10.0

The above ingredients are blended until a homogeneous solution results.

EXAMPLE 3

	Percent
Product of Example 1	35.0
Dimethyl formamide	65.0

The active compound is blended with the dimethyl formamide until a homogeneous solution results.

EXAMPLE 4

	Percent
3-dimethylamino-5-(N-ethoxy-N-methylamino)-1,2,4-dithiazolium chloride	95.0
Sodium dioctyl sulfosuccinate	0.5
Synthetic silica	4.5

The above ingredients are blended, ground to pass an 0.50 mm screen and reblended.

EXAMPLE 5

	Percent
3,5-bis(N-methoxy-N-methylamino)-1,2,4-dithiazolium chloride	80.0
Kaolinite clay	18.5
Sodium lignin sulfonate	0.5
Sodium alkylnaphthalene sulfonate	1.0

The above ingredients are blended, micropulverized to pass an 0.149 mm screen and reblended.

EXAMPLE 6

	Percent
3-diethylamino-5-(N-methoxy-N-methylamino)-1,2,4-dithiazolium bisulfite	50.0
Sucrose	49.0
Methylated cellulose	0.5
Sodium dioctyl sulfosuccinate	0.5

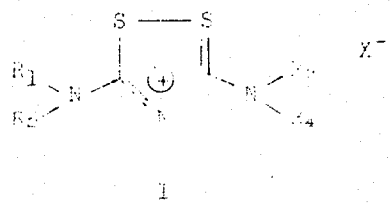
The above ingredients are blended, ground to pass an 0.30 mm screen and reblended.

EXAMPLE 7

The foliage of two Red Kidney bean plants was infested with approximately 200 mites (50 per leaf) and then sprayed to run-off with a solution containing 50 ppm of 3-dimethylamino-5-(N-methoxy-N-methyl)-1,2,4-dithiazolium bromide. No living mites could be found on these plants one week after treatment.

I claim:

1. Compounds of formula



I

where

R_1 and R_3 are C_1–C_2 alkyl;

R_2 is C_1–C_2 alkyl or C_1–C_2 alkoxyl;

R_4 is C_1–C_2 alkoxyl; and

X^- is an anion of the corresponding acid HX having an ionization contant of at least 1×10^{-7}.

2. Compounds of formula I wherein R_1, R_2, and R_3 are C_1–C_2 alkyl and R_4 is C_1–C_2 alkoxyl.

3. Compound of claim **1** which is 3-dimethylamino-5-(N-methoxy-N-methylamino)-1,2,4-dithiazolium bromide.

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