

[54] 2-SULPHENYLIMINO-5-AMINO-1,3-DITHIANES

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[51] Int. Cl..... **C07d 29/36**

[58] Field of Search.... **260/293.68, 327 M, 247.1 P, 260/268 S, 326.84**

[56] **References Cited**

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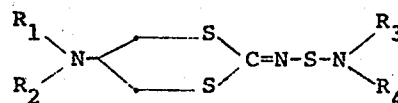
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[57] **ABSTRACT**

The present invention concerns novel 5-amino-1,3-dithiane derivatives of the formula:



wherein

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are substituents such as alkyl.

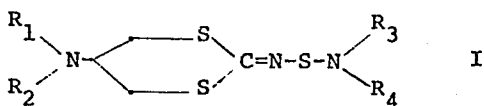
The compounds are useful insecticides.

**12 Claims, No Drawings**

## 2-SULPHENYLIMINO-5-AMINO-1,3-DITHIANES

The present invention relates to sulphur containing heterocyclic compounds and more specifically to 5-amino-1,3-dithiane derivatives possessing insecticidal properties.

Accordingly the present invention provides compounds of formula I,



wherein

$R_1$  is alkyl of 1 to 5 carbon atoms,

$R_2$  is hydrogen or alkyl or 1 to 5 carbon atoms, and either

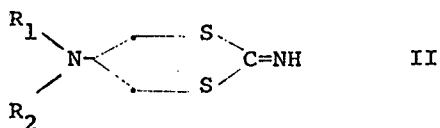
$R_3$  and  $R_4$  are each, independently, alkyl of 1 to 5 carbon atoms, or

$R_3$  and  $R_4$ , together with the nitrogen atom to which they are bound, form a 5 to 6 membered heterocyclic ring containing 1 or 2 hetero atoms.

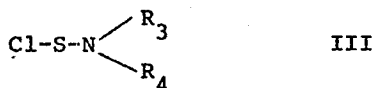
When any or all of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are alkyl of over 2 carbon atoms, this may be branched or straight chain, a primary or secondary alkyl and when of over 3 carbon atoms, the alkyl may be tertiary alkyl. When any or all of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are alkyl, this is preferably of 1, 2, 3 or 4 carbon atoms, e.g. methyl, ethyl, n-propyl, n-butyl or sec.butyl.

When  $R_3$  and  $R_4$  together with the nitrogen atom to which they are bound, form a 5 to 6 membered heterocyclic ring, this preferably contains one nitrogen hetero atom, two nitrogen hetero atoms or one nitrogen hetero atom and one oxygen hetero atom. Examples of heterocyclic rings formed by  $R_3$  and  $R_4$ , together with the nitrogen atom to which they are bound, are piperidino, pyrrolidino, piperazino and morpholino, particularly the 6 membered heterocyclic rings.

The present invention also provides a process for the production of a compound of formula I which comprises condensing a compound of formula II



wherein  $R_1$  and  $R_2$  are as defined above, with a compound of formula III,



wherein  $R_3$  and  $R_4$  are as defined above.

The compounds of formula I may exist in either free base or acid addition salt form. Acid addition salt forms may be produced from free base forms in manner known per se and vice versa.

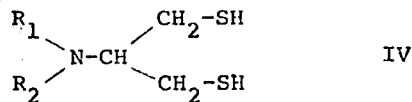
The process of the invention may, for example, be effected as follows viz:

A compound of formula II is conveniently reacted with stirring, with a compound of formula III, over a period of 2 to 6 hours, e.g. 3 hours, in an appropriate anhy-

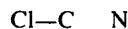
drous solvent, such as a nitrile, e.g. acetonitrile. An acid acceptor, e.g. triethylamine is preferably employed, especially if the compound of formula II is employed in acid addition salt form, in which case, an excess of acid acceptor is preferably employed.

Working up is effected in conventional manner.

The compounds of formula II, employed as starting material in the process of the present invention may, for example, be produced by condensing a compound of formula IV,



wherein  $R_1$  and  $R_2$  are as defined above, with a compound of formula V,



in an inert atmosphere.

The reaction may be effected by dissolving a compound of formula IV in a solvent such as chloroform, in an inert atmosphere such as nitrogen, and passing the chlorocyanide through the solution at a slightly elevated temperature, e.g. between 40° and 50°C over a period of between 4 and 8 hours, e.g. 5 to 6 hours, preferably with stirring.

Working up may be effected in conventional manner.

The compound of formula I possess insecticidal activity as indicated by an insecticidal effect in the following tests viz:

## Test (i)

Insecticidal effect against *Bruchidius obtectus* (bean weevil) — contact effect

Petri dishes having a diameter of 7 cm are coated by spraying with 0.1 to 0.2 cc of an emulsion containing 0.2 % of a compound of formula I, e.g. 2-dimethylaminosulphenylimino-5-dimethylamino-1,3-dithiane, 2-di-n-propylaminosulphenylimino-5-dimethylamino-1,3-dithiane, hydrogenoxalate of the 2-di-n-propylaminosulphenylimino-5-dimethylamino-1,3-dithiane, 2-di-n-butylaminosulphenylimino-5-dimethylamino-1,3-dithiane and 2-di-sec-butylaminosulphenylimino-5-dimethyl amino-1,3-dithiane. After drying the coating for about 4 hours, 10 *Bruchidius imago*s are placed in each dish which is covered with a lid comprising a fine mesh brass wire grid. The insects are kept without food at room temperature. After 48 hours the rate of mortality is determined.

## Test (ii)

Insecticidal effect against *Ephestia kuehniella* (flour moth) — contact effect

Petri dishes having a diameter of 6 cm, each containing 10 caterpillars 10 to 12 mm in length, are coated by spraying with 0.1 to 0.2 cc of an emulsion containing 0.05 % of a compound of formula I, e.g. 2-dimethylaminosulphenylimino-5-dimethylamino-1,3-dithiane, 2-di-n-propylaminosulphenylimino-5-dimethylamino-1,3-dithiane, hydrogenoxalate of the 2-di-n-propylaminosulphenylimino-5-dimethylamino-

1,3-dithiane, 2-di-n.butylaminosulphenylimino-5-dimethylamino-1,3-dithiane, hydrogenoxalate of the 2-di-n.butylaminosulphenylimino-5-dimethylamino-1,3-dithiane, and 2-si-sec.-butylaminosulphenylimino-5-dimethylamino-1,3-dithiane. The dishes are then covered with a fine mesh brass wire grid. After drying the coating a wafer is given as food and renewed as required. After 5 days the rate of mortality is determined by counting the live and dead insects.

Furthermore, the compounds possess low toxicity in warm blooded animals as indicated by LD<sub>50</sub> determinations on male white rats.

The compounds are therefore useful as insecticides particularly in animal buildings e.g. stables, in houses e.g. in cellars and attics thereof, and in plant loci.

For the abovementioned use the amount of the compound to be applied will vary depending on the particular compound employed, the mode of application, ambient conditions and the effect desired. With regard to plant protection, in general, an indicated amount to be applied to a plant locus is between 200g and 5 Kg/hectare.

The compounds may be employed as a composition with insecticidal or fungicidal carriers and diluents in solid or liquid form e.g. spraying and dusting powders, strewing granulates, spraying liquids and aerosols.

Solid forms may include diluents and carriers such as diatomaceous earth, talc, kaolinite, attapulgit, pyrophyllite, artificial mineral fillers based on SiO<sub>2</sub> and silicates, limestone, decahydrate and plant material carriers such as walnut and flour. Adjuvants e.g. surfactants such as wetting and dispersing agents, e.g. sodium lauryl sulphate, sodium dodecyl benzenesulphonate, condensation products from naphthalene sulphonate and formaldehyde, polyglycol ether and lignin derivatives such as sulphite liquor, may also be included in the case of wettable powders to be applied as a water suspension. Granulates are produced by coating or impregnating granular carrier materials such as pumice, limestone, attapulgit and kaolinite with the compounds.

Liquid forms may include non-phytotoxic diluents and carriers such as alcohols, glycolic ethers, aliphatic and aromatic hydrocarbons e.g. xylene, alkyl naphthalenes and other petroleum distillates, and ketones e.g. cyclohexanone and isophorone. Adjuvants such as surface active agents, e.g. wetting and emulsifying agents such as polyglycol ether formed by the reaction of an alkylene oxide with high molecular weight alcohols, mercaptans or alkyl phenols, and/or alkyl benzene sulphonates, may be included in emulsion concentrate forms.

Aside from the abovementioned carriers, diluents and adjuvants, adjuvants, such as stabilizing agents, desactivators (for solid forms with carriers having an active surface), agents for improving adhesiveness to surfaces treated, anticorrosives, defoaming agents and pigments may also be included.

Concentrate forms of composition generally contain between 1 and 5 percent preferably between 5 and 50 percent by weight of active compound.

Application forms of composition generally contain between 0.01 and 95 percent, preferably between 0.01 and 20 percent by weight of active compound.

Examples of concentrate forms of composition will now be described.

#### a. Emulsifiable concentrate

25 parts by weight of an active agent of formula I, 5 parts by weight of a condensation product form formaldehyde and naphthalene sulphonate, 2 parts by weight of dextrin, 1 part by weight of ammonium caseinate and 62 parts by weight of diatomaceous earth are mixed until a homogeneous mixture is obtained, and this is then ground until the particles are considerably smaller and 45 microns as an average. Before application the powder is diluted with water to the desired concentration.

#### b. Emulsifiable concentrate

25 parts by weight of an active agent of formula I are mixed with 25 parts by weight of an alkylphenolethylene oxide adduct (with approximately 10 ml of ethylene oxide) and 50 parts by weight of acetone. Before application, the concentrate is diluted with water to the desired concentration.

#### c. Emulsifiable concentrate

50 parts by weight of a compound of formula I are mixed with 50 parts by weight of sodium-lauryl sulphate, 3 parts by weight of sodium-lignine sulphonate and 45 parts by weight of kaolinite. The concentrate is diluted with water to the desired concentration before application.

Free base and acid addition salt forms of the compounds of formula I exhibit the same order of activity. Examples of agriculturally acceptable acid addition salt forms are the acetates, benzoates, hydrogen oxalates, hydrochlorides and hydrogen sulphates.

A preferred group of compounds of formula I are the compounds wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> of formula I are each alkyl of 1 to 4 carbon atoms.

Another preferred group of compounds of formula I are the compounds wherein R<sub>1</sub> and R<sub>2</sub> of formula I are each alkyl, and R<sub>3</sub> and R<sub>4</sub> together with the nitrogen atom to which they are bound form a piperidino, piperazino or a morpholino heterocyclic ring, especially a piperidino ring.

Examples of the process for producing the compounds of the invention will now be described in more detail. Where temperature is referred to, this is in °C.

### I. FINAL COMPOUNDS

#### EXAMPLE 1

##### 2-Di-n.butylaminosulphenylimino-5-dimethylamino-1,3-dithiane

7.5 g (0.03 mol) of 2-Imino-5-dimethylamino-1,3-dithiane-bis-hydrochloride are suspended in 100 cc of absolute acetonitrile and to the suspension are added 9.8 g (0.05 mol) of di-n.butylamidodisulphenylchloride, which is diluted with 50 cc of absolute acetonitrile. 12.2 g (0.12 mol) of triethylamine in 50 cc of absolute acetonitrile are added dropwise, whilst stirring, to this mixture. The temperature rises slightly and after approximately 60 minutes the dropwise addition is complete. The mixture is stirred for 3 further hours without heating and the obtained triethylamine hydrochloride is then suction filtered. The solvent is eliminated and an oil is obtained from the filtrate. The oil is taken up in chloroform, washed twice with a small amount of water and after distillation of the chloroform in a high vac-

uum, over the course of 30 minutes, at 50°C, liberated from impurities.

Analysis:  $C_{14}H_{29}N_3S_3$ ; Molecular weight: 335;

Calcd.: C 50.1%; H 8.7%; N 12.5%; S 28.7%.

Found: C 50.7%; H 9.3%; N 11.3%; S 28.0%.

### EXAMPLE 2

2-Di-n-butylaminosulphenylimino-5-dimethylamino-1,3-dithiane (hydrogen oxalate form)


1.2 g (0.0135 mol) of anhydrous oxalic acid in 20 cc of absolute ethanol are added to 4.0 g (0.012 mol) of 2-di-n-butylaminosulphenylimino-5-dimethylamino-1,3-dithiane in 10 cc of absolute ethanol. The precipitated crystalline product is filtered and washed with a small amount of alcohol. The salt is dried in a vacuum at 50° and colourless crystals, having a M.P. of 185° (decomposition), are obtained.

Analysis:  $C_{16}H_{31}N_3O_4S_3$ ; Molecular weight: 425;

Calcd.: C 45.2%; H 7.3%; N 9.9%; S 22.6%.

Found: C 44.9%; H 7.4%; N 9.4%; S 22.5%.

The following compounds of formula I may be produced in analogous manner to that described in Examples 1 and 2:

Example No.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Salt	Empirical formula Molecular weight	M.P. [°C] Ref.	Analysis % Calc. Found
3	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	-	$C_8H_{17}N_3S_3$ 251	liquid	C 38.3 % 38.1 % H 6.8 % 6.5 % N 16.7 % 16.3 % S 38.3 % 39.9 %
4	CH <sub>3</sub>	CH <sub>3</sub>	n-C <sub>3</sub> H <sub>7</sub>	n-C <sub>3</sub> H <sub>7</sub>	-	$C_{12}H_{25}N_3S_3$ 307	liquid	C 46.9 % 47.5 % H 8.2 % 8.6 % N 13.7 % 13.1 % S 31.2 % 30.1 %
5	CH <sub>3</sub>	CH <sub>3</sub>	n-C <sub>3</sub> H <sub>7</sub>	n-C <sub>3</sub> H <sub>7</sub>	hydrogen oxalate	$C_{14}H_{27}N_3O_4S_3$ 397	171°	C 42.3 % 41.8 % H 6.8 % 6.8 % N 10.6 % 10.2 % S 24.2 % 23.9 %
6	CH <sub>3</sub>	CH <sub>3</sub>	sec-C <sub>4</sub> H <sub>9</sub>	sec-C <sub>4</sub> H <sub>9</sub>	-	$C_{14}H_{29}N_3S_3$ 335	liquid	C 50.1 % 51.3 % H 8.7 % 9.0 % N 12.5 % 11.8 % S 28.7 % 28.2 %
7	CH <sub>3</sub>	CH <sub>3</sub>			-	$C_{11}H_{21}N_3S_3$ 291	liquid R <sub>F</sub> =0.65*	C 45.2 % 45.2 % H 7.2 % 7.6 % N 14.4 % 13.0 % S 33.0 % 32.1 %

\*) R<sub>F</sub>-value, thin layer chromatography on silica gel G with acetone as eluant

## II. STARTING MATERIALS

The starting materials of formula II may be produced in accordance with the following Example:

Production of the  
2-imino-5-dimethylamino-1,3-dithiane-(bis-hydrochloride form)

The following processes are effected in an atmosphere of nitrogen:

47 g (0.2 mol) of 1,3-bis-acetylthio-2-dimethylaminopropane are added to a solution of 0.8 g of sodium metal in 800 cc of absolute methanol and the mixture is subsequently boiled at reflux for 4 hours. The methanol is completely distilled off and the remaining residue is dissolved in 1000 cc of chloroform,

cooled to 0°-10°, and hydrogen chloride is passed through until an excess of at least 0.2 mol of hydrochloric acid is dissolved in chloroform. 6 cc of ethanol are added. Chlorocyanide is passed through the chloroform solution at 40°-50° during approximately 5 hours, while stirring vigorously and the mixture is then stirred for one further hour at 40°-50°. After cooling, the main part of the excess chlorocyanide is removed by blowing nitrogen through the solution and the precipitated salt, which is washed with methanol, is collected. After drying in a high vacuum at 50°, colourless crystals are obtained which may be recrystallized from methanol. M.P. 243°-45°.

Analysis:  $C_6H_{12}N_2S_2 \cdot 2 HCl$ ; Molecular weight: 249;

Calcd.: C 28.9%; H 5.6%; N 11.2%; S 25.7%;

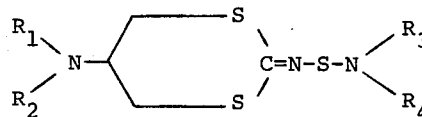
28.5%.

Found: C 29.4%; H 5.5%; N 11.4%; S 26.1%;

28.5%.

What is claimed is:

1. A compound of the formula:



wherein

R<sub>1</sub> is alkyl of 1 to 5 carbon atoms,

R<sub>2</sub> is hydrogen or alkyl of 1 to 5 carbon atoms, and

R<sub>3</sub> and R<sub>4</sub> are independently alkyl or 1 to 5 carbon atoms or together with the nitrogen atom to which they are bound form piperidino, pyrrolidino, piperazino or morpholino,

in free base or agriculturally acceptable acid addition salt form.

2. A compound of claim 1, wherein R<sub>1</sub> and R<sub>2</sub> are each independently, alkyl of 1 to 5 carbon atoms.

3. A compound of claim 2, wherein R<sub>3</sub> and R<sub>4</sub> are each independently alkyl of 1 to 5 carbon atoms.

4. The compound of claim 3, which is 2-di-n-butylaminosulphenylimino-5-dimethylamino-1,3-dithiane.

5. The compound of claim 3, which is 2-dimethylaminosulphenylimino-5-dimethylamino-1,3-dithiane.

6. The compound of claim 3, which is 2-di-n-propylaminosulphenylimino-5-dimethylamino-1,3-dithiane.

7. The compound of claim 3, which is 2-di-sec-butylaminosulphenylimino-5-dimethylamino-1,3-

dithiane.

8. A compound of claim 2, wherein R<sub>3</sub> and R<sub>4</sub>, together with the nitrogen atom to which they are bound form a piperidino, pyrrolidino, piperazino or morpholino ring.

9. A compound of claim 8, wherein R<sub>3</sub> and R<sub>4</sub>, together with the nitrogen to which they are bound, form a piperidino ring.

10. The compound of claim 9, which is 2-piperidinosulphenylimino-5-dimethylamino-1,3-dithiane.

11. A compound of claim 1, in acid addition salt form.

12. A compound of claim 11, in agriculturally acceptable hydrogen oxalate form.

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