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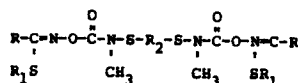
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54 Substituted carbamates, preparation thereof and use thereof as insecticides.

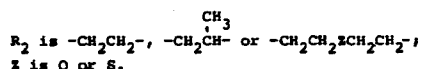
57 Substituted carbamates, preparation thereof and use thereof as insecticides, for control of pestiferous insects belonging to such orders as Lepidoptera, Coleoptera and Diptera, the carbamates having the formula:



wherein

R is branched or straight chain alkyl containing 1 to 3 carbon atoms or methoxymethyl;

R₁ is branched or straight chain alkyl containing 1 to 3 carbon atoms;



An illustrative compound is dimethyl-N,N'- [[1,2-ethanediylbis [thio(methylimino) carbonyloxy]] bis (ethaneimidothioate).

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Substituted carbamates, preparation thereof and use thereof as insecticides.

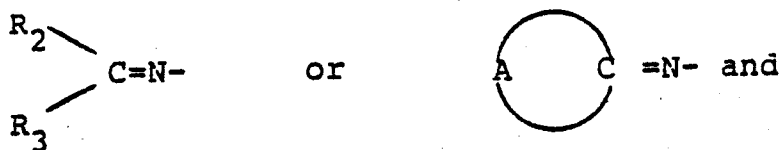
This invention relates to substituted carbamates, preparation thereof and use thereof as insecticides for the control of pestiferous insects.

Belgian Patent No. 848,912, granted May 21, 1977, relates to insecticidal symmetrical bis-carbamoyl sulfide compounds of the following general formula:



10 wherein:

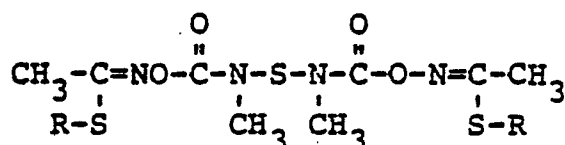
R is:



R' is alkyl containing from one to four carbon atoms. Among the numerous compounds which are included in the Belgian Patent are those wherein R₂ is alkyl, optionally substituted with one or more alkylthio groups, and wherein R₃ is hydrogen alkyl or alkoxy. The patentee states, however, that while compounds according to the above formula wherein R₂ is an

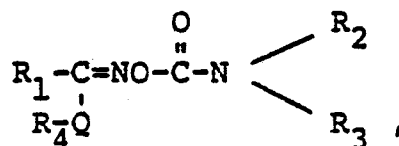
alkylthioalkyl substituent and R_3 is hydrogen exhibit good pesticidal activity, their mammalian toxicity is unacceptably high.

U.S. Patent 4,004,031 issued January 18, 1977,
5 discloses insecticidal compounds of the formula:



wherein R is an alkyl group of one to five carbons.

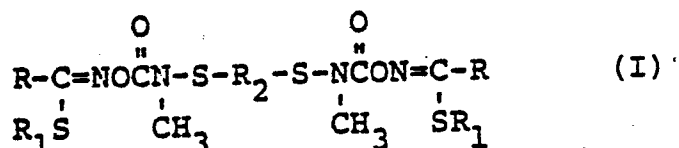
10 U.S. Patent 3,576,834 issued April 27, 1971,
relates to insecticidal compounds having the structure:



15

such as methomyl.

This invention relates to compounds of Formula I,
their preparation, to insecticidal compositions containing
them and to the method of using said compounds as
20 insecticides.



wherein

R is a branched or straight chain alkyl group
of 1-3 carbon atoms or CH_2OCH_3 ;

25 R_1 is a branched or straight chain alkyl group
of 1-3 carbon atoms;

R_2 is $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\overset{\text{CH}_3}{\text{CH}}-$ or $-\text{CH}_2\text{CH}_2\text{ZCH}_2\text{CH}_2-$; and
Z is oxygen or sulfur.

Compounds which are preferred for their high
30 insecticidal activity are those compounds of Formula I
wherein

where R is methyl or ethyl; and

R₁ is methyl.

More preferred for their higher insecticidal activity are those compounds of Formula I wherein

5 R is methyl;

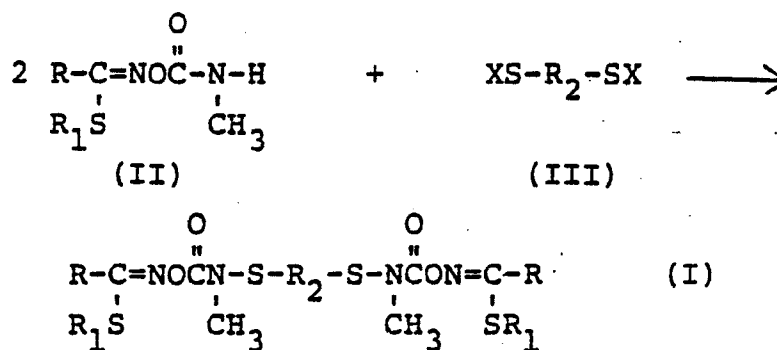
R₁ is methyl; and

R₂ is -CH₂CH₂-.

Specifically preferred for its outstanding insecticidal activity is dimethyl N,N'[[1,2-ethane-
10 diylbis[thio(methylimino)carbonyloxy]]]bis(ethane-imidothioate).

The compounds of Formula I can be prepared, as shown in Equation A, by reacting preferably at least two moles of a substituted N-(aminocarbonyloxy)-alkanimidothioic
15 acid ester of Formula II with one mole of an alkane disulphenyl halide of Formula III in the presence of a base:

Equation A



20 wherein R, R₁, and R₂ are as previously defined and X is halogen.

The reaction can be carried out in any organic solvent which is inert to the reactants and the reaction products, e.g. methylene chloride, dioxane, tetrahydro-
25 furan, chloroform, 1,2-dichlorethane, acetonitrile, benzene, toluene, the xylenes, acetone or methyl ethyl ketone. Mixtures of such solvents can also be used.

A base which will function as an acid acceptor can be used in synthesizing the compounds of this invention.

The process can be carried out at a temperature of between about -20° and 60°C, preferably between about -5° and 40°C. Pressure is not critical; for convenience, atmospheric pressure is preferred.

Preparation of the compounds of Formula II used as starting materials is described in U.S. Patents 3,574,736; 3,576,834 and 3,787,470.

10 In the compounds of Formula III, chlorine is the preferred halogen for economic reasons, and those compounds can be prepared by a suitable modification of the methods described in the Journal of Heterocyclic Chemistry, 6, 629 (1969). Alkane sulfenyl halides, 15 such as those of Formula III wherein X is fluorine, bromine, or iodine, are also known and may be prepared by the methods reviewed in Synthesis, 11, 561-580 (1970).

In the examples which follow, which are illustrative only, temperatures are given in degrees centigrade.

Example 1

Ethane-1,2-bisthioacetate

To a solution of 141 g of sodium methoxide in 1 l of absolute ethanol, under a dry nitrogen atmosphere, 25 was added 200 g of thiolacetic acid dropwise with stirring over a period of 20 minutes. Ethylene dibromide (229.2 g) was then added and the reaction heated to reflux for five hours. The reaction mixture was cooled, sodium bromide was filtered off, and the 30 ethanol was removed under vacuum. The residue was taken up in diethyl ether, washed with water, dried over anhydrous magnesium sulfate and the crude product isolated by distillation of the diethyl ether solvent. After recrystallization from hexanes, the product, 35 ethane-1,2-bisthiolacetate, melted at 68-70°.

Example 2Ethane-1,2-Disulfenyl Chloride

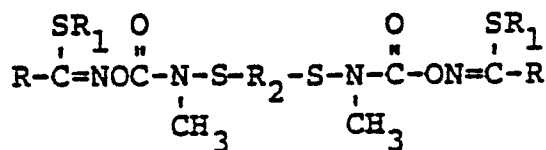
Sulfuryl chloride (54 g) was added dropwise to a solution of 35.6 g of ethane-1,2-bisthiolacetate in 200 ml of methylene chloride at ambient temperature. After stirring for 45 minutes at room temperature the methylene chloride solvent and volatile by-products were removed by vacuum distillation of 0°. The yellow product, ethane-1,2-disulfenyl chloride, melted at 32-34°.

Example 3Dimethyl N,N'[[1,2-ethanediy]bis[thio(methylimino)-carbonyloxy]]bis(ethanimidothioate)

A solution of 6.5 g of N-(methylaminocarbonyloxy)-ethanimidothioic acid, methyl ester, in 50 ml methylene chloride and 2.0 ml of pyridine was prepared. To that solution was added dropwise 28 gm of ethane-1,2-disulfenyl chloride, dissolved in 25 ml of methylene chloride, with stirring over a period of 10 minutes. The reaction was slightly exothermic. After stirring for about 16 hours at ambient temperature, the reaction mixture was washed with water, dried over anhydrous magnesium sulfate, and the crude product isolated by distilling off the methylene chloride solvent. After recrystallization from ethyl alcohol followed by recrystallization from acetonitrile, the product, dimethyl N,N'-[[1,2-ethanediy]bis[thio(methylimino)carbonyloxy]]bis(ethanimidothioate), melted at 176-179°.

By reacting equivalent amounts of other compounds of Formula II with compounds of Formula III using the procedures of Examples 1, 2, and 3, the following compounds of Formula I can be prepared.

Table I



I. 2.11.11

5

	<u>R</u>	<u>R₁</u>	<u>R₂</u>
	CH ₃	C ₂ H ₅	-CH ₂ CH ₂ -
	CH ₃	nC ₃ H ₇	-CH ₂ CH ₂ -
10	CH ₃	i-C ₃ H ₇	-CH ₂ CH ₂ -
	CH ₃ OCH ₂	CH ₃	-CH ₂ CH ₂ -
	C ₂ H ₅	CH ₃	-CH ₂ CH ₂ -
	nC ₃ H ₇	CH ₃	-CH ₂ CH ₂ -
	i-C ₃ H ₇	CH ₃	-CH ₂ CH ₂ -
15	C ₂ H ₅	C ₂ H ₅	-CH ₂ CH ₂ -
	C ₂ H ₅	i-C ₃ H ₇	-CH ₂ CH ₂ -
	C ₂ H ₅	n-C ₃ H ₇	-CH ₂ CH ₂ -
	n-C ₃ H ₇	C ₂ H ₅	-CH ₂ CH ₂ -
	i-C ₃ H ₇	C ₂ H ₅	-CH ₂ CH ₂ -
20	CH ₃	CH ₃	-CH ₂ CH ₂ OCH ₂ CH ₂ -
	CH ₃	C ₂ H ₅	-CH ₂ CH ₂ OCH ₂ CH ₂ -
	C ₂ H ₅	CH ₃	-CH ₂ CH ₂ OCH ₂ CH ₂ -
	CH ₃	CH ₃	-CH ₂ CH ₂ SCH ₂ CH ₂ -

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Formulation

Useful formulations of the compounds of Formula I can be prepared in conventional ways. They include dusts, granules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates and the like. Many of these may be applied directly. Sprayable formulations can be extended in suitable media and used at spray volumes of from a few pints to several hundred gallons per acre. High strength compositions are primarily used as intermediates for further formulation. The formulations, broadly, contain e.g. about 1% to 99% by weight of active ingredient(s) and at least one of (a) e.g. about 0% to 20% surfactant(s) and (b) e.g. about 1% to 99% solid or liquid diluent(s). More specifically, they will contain these ingredients in the following approximate proportions:

Percent by Weight*			
	Active Ingredient	Diluent(s)	Surfactant(s)
Wettable Powders	20-90	0-74	1-10
20 Oil Suspensions	5-50	40-95	0-15
Emulsions, Solutions, (including Emulsifiable Concentrates)			
25 Aqueous Suspensions	10-50	40-84	1-20
Dusts	1-25	70-99	0-5
Granules and Pellets	1-95	5-99	0-15
High Strength Compositions	90-99	0-10	0-2

30 *Active Ingredient plus at least one of a Surfactant or Diluent equals 100 weight percent.

Lower or higher levels of active ingredient can, of course, be present depending on the intended use and the physical properties of the compound. Higher ratios of surfactant to active ingredient are sometimes

desirable, and are achieved by incorporation into the formulation or by tank mixing.

- Typical solid diluents are described in Watkins, et al., "Handbook of Insecticide Dust Diluents and Carriers," 2nd Edn., Dorland Books, Caldwell, N.J.
- The more absorptive diluents are preferred for wettable powders and the denser ones for dusts. Typical liquid diluents and solvents are described in Marsden, "Solvents Guide," 2nd Edn., Interscience, New York, 1950. Solubility under 0.1% is preferred for suspension concentrates; solution concentrates are preferably stable against phase separation at 0°C. "McCutcheon's Detergents and Emulsifiers Annual," McCutcheon Division, MC Publishing Co., 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.
- The methods of making such compositions are well known. Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer or fluid energy mill. Suspensions are prepared by wet milling (see, for example, Littler, U.S. Patent 3,060,084). Granules and pellets may be made by spraying the active material upon preformed granular carriers or by agglomeration techniques.

- See J. E. Browning, "Agglomeration," Chemical Engineering, Dec. 4, 1967, pp. 147ff. and "Perry's Chemical Engineer's Handbook," 4th Edn., McGraw-Hill, N.Y., 1963, pp. 8-59ff.

For further information regarding the art of formulation, see for example:

10 01

J. B. Buchanan, U.S. Patent 3,576,834
 April 27, 1971, Col. 5, line 36 through
 Col. 7, line 70 and Exs. 1-4, 17, 106,
 123-140.

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R. R. Shaffer, U.S. Patent 3,560,616,
 Feb. 2, 1971, Col. 3, line 48 through
 Col. 7, line 26 and Exs. 3-9, 11-18.

E. Somers, "Formulation," Chapter 6 in
 Torgeson, "Fungicides," Vol. I,
 Academic Press, New York, 1967.

Example 4

10 Wettable Powder

Dimethyl N,N'-[[1,2-ethanediy]bis[thio(methylimino)-	
carbonyloxy]]]bis(ethanimidothioate)	40.0%
dioctyl sodium sulfosuccinate	1.5%
sodium ligninsulfonate	3.0%
15 low viscosity methyl cellulose	1.5%
attapulgit	54.0%

The ingredients are thoroughly blended, passed
 through an air mill, to produce an average particle
 size under 15 microns, reblended, and sifted through
 20 a U.S.S. No. 50 sieve (0.3 mm opening) before
 packaging.

All compounds of the invention may be formulated
 in the same manner.

Example 5

25 Wettable Powder

Dimethyl N,N'-[[1,2-ethanediy]bis[thio(methylimino)-	
carbonyloxy]]]bis(ethanimidothioate)	50.0%
sodium alkylnaphthalenesulfonate	2.0%
low viscosity methyl cellulose	2.0%
30 diatomaceous earth	46.0%

The ingredients are blended, coarsely hammer
 milled and then air milled to produce particles of
 active ingredient essentially all below 10 microns in
 diameter. The product is reblended before packaging.

Lofaregana

Example 6Wettable Powder

Dimethyl N,N'-[[1,2-ethanediylbis[thio(methylimino)-
carbonyloxy]]]bis(ethanimidothioate) 65.0%

5 dodecylphenol polyethylene glycol
ether 2.0%

sodium ligninsulfonate 4.0%

sodium silicoaluminate 6.0%

montmorillonite (calcined) 23.0%

10 The ingredients are thoroughly blended. The
liquid surfactant is added by spraying upon the
solid ingredients in the blender. After grinding in
a hammer mill to produce particles essentially all
below 100 microns, the material is reblended and
15 sifted through a U.S.S. No. 50 sieve (0.3 mm opening)
and packaged.

Example 7Aqueous Suspension

Dimethyl N,N'-[[1,2-ethanediylbis[thio(methylimino)-
20 carbonyloxy]]]bis(ethanimidothioate) 25.0%

hydrated attapulgite 3.0%

crude calcium ligninsulfonate 10.0%

sodium dihydrogen phosphate 0.5%

water 61.5%

25 The ingredients are ground together in a ball or
roller mill until the solid particles have been
reduced to diameters under 10 microns.

Example 8Oil Suspension

30 Dimethyl N,N'-[[1,2-ethanediylbis[thio(methylimino)-
carbonyloxy]]]bis(ethanimidothioate) 25.0%

polyoxyethylene sorbitol hexaoleate 5.0%

highly aliphatic hydrocarbon oil 70.0%

The ingredients are ground together in a sand
35 mill until the solid particles have been reduced to

under about 5 microns. The resulting thick suspension may be applied directly, but preferably after ~~being~~ extended with oils or emulsified in water.

Example 9

5 Granule

wettable powder of Example 4	10.0%
attapulgite granules	90.0%
(U.S.S. No. 20-40; 0.84-0.42 mm)	

A slurry of wettable powder containing 50% solids is sprayed on the surface of attapulgite granules in a double-cone blender. The granules are dried and packaged.

Example 10

Extruded Pellet

15	Dimethyl N,N'-[[1,2-ethanediylbis[thio(methylimino)-carbonyloxy]]]bis(ethanimidothioate)	25.0%
	anhydrous sodium sulfate	10.0%
	crude calcium ligninsulfonate	5.0%
	sodium alkyl naphthalenesulfonate	1.0%
20	calcium/magnesium bentonite	59.0%

The ingredients are blended, hammer-milled and then moistened with about 12% water. The mixture is extruded as cylinders about 5 mm diameter which are cut to produce pellets about 3 mm long. These may be crushed to pass a U.S.S. No. 20 sieve (0.84 mm opening). The granules held on a U.S.S. No. 40 sieve (0.42 mm opening) may be packaged for use and the fines recycled.

Example 11

30 High Strength Concentrate

	Dimethyl N,N'-[[1,2-ethanediylbis[thio(methylimino)-carbonyloxy]]]bis(ethanimidothioate)	98.5%
	silica aerogel	0.5%
	synthetic amorphous fine silica	1.0%

The ingredients are blended and ground in a hammer mill to produce a high-strength concentrate essentially all passing a U.S.S. No. 50 sieve (0.3 mm opening). This material may then be formulated in a variety of ways.

Example 12

Dust

	high-strength concentrate, Example 11	25.4%
10	pyrophyllite, powdered	74.6%

The ingredients are thoroughly blended and packaged for use.

Example 13

Emulsifiable Concentrate

15	Dimethyl N,N'[[1,2-ethanediy]bis[thio(methylimino)- carbonyloxy]]bis(ethanimidothioate)	20.0%
	chlorobenzene	74.0%
	sorbitan monostearate and polyoxyethylene condensates thereof	6.0%
20	The ingredients are combined and stirred to produce a solution which can be emulsified in water for application.	

Example 14

Emulsifiable Concentrate

25	Dimethyl N,N'-[[1,2-ethanediy]bis[thio(methylimino)- carbonyloxy]]bis(ethanimidothioate)	10.0%
	blend of oil-soluble sulfonates and polyoxyethylene ethers	10.0%
	xylene	80.0%
30	The ingredients are combined and stirred with gentle warming to speed solution. A fine screen filter is included in packaging operation to ensure the absence of any extraneous undissolved material in the product.	

Use

The compounds of this invention are useful for control of insects which are detrimental to agriculture.

- 5 As demonstrated in Examples 16 to 18 below, improved residual insecticidal properties as well as decreased phytotoxicity are obtained with a formulation containing a compound of Formula I.

The compounds readily control pestiferous insects
10 belonging to such orders as Lepidoptera, Coleoptera, and Diptera. More specifically, insects controlled by the compounds of this invention include but are not limited to: cotton bollworm (Heliothis zea), tobacco budworm (Heliothis virescens), southern armyworm
15 (Spodoptera eridania), beet armyworm (Spodoptera exigua), soybean looper (Pseudoplusia includens), Mexican bean beetle (Epilachna varivestis), and the house fly (Musca domestica).

The insects are controlled by applying the
20 compound to the locus of infestation, to the area to be protected, or to the pests themselves. For the control of insects in agricultural crops, a compound of Formula I is generally applied to the foliage or other plant parts which are infested or
25 which are to be protected. Effective amounts to be applied depend upon the species to be controlled, its life stage, its size and location, the amount of rainfall, the time of year, moisture, temperature, type of application, and other variables. In general,
30 0.1 to 10 kg/ha may be required for insect control in agriculture with rates of .2 to 4 kg/ha usually being sufficient in many situations. In large-scale field operations, rates in the range of 1/4 to 2 kg/ha are generally used.

The compounds of this invention will generally be used in formulation with a carrier that commonly will contain oil or water. Applications may be made with concentrated or dilute suspensions of the insecticide in the carrier. Low-volume applications utilizing dispersions containing about 20% of the active ingredient may be preferred by some applicators while others may prefer dilute suspensions containing only 25 ppm in high-volume applications.

10 The compounds of this invention possess significant advantages over prior art compounds, e.g. fewer applications are required to provide a given level of insect control due to this distinctly longer residual insecticidal action. Use of fewer applications results in greater economy to the grower and dissemination of less insecticide in the environment. An additional advantage is lower phytotoxicity to cotton.

Conventionally, the compounds will be incorporated into a formulation in a known manner with incorporation of other components such as (a) surfactants, (b) diluents, (c) additives to reduce foam or corrosion, or (d) preservatives to control microbiological growth.

The compounds of this invention can be mixed with fungicides, bactericides, acaricides, nematocides, other insecticides, or other biologically active compounds in order to achieve desired results with a minimum expenditure of time, effort and material. Amounts of these biologically active materials added for each part by weight of the composition of this invention may vary from 0.05 to 25 parts by weight. Suitable agents of this type are well-known to those skilled in the art. Some are listed below:

Fungicides:

- 1 methyl 2-benzimidazolecarbamate;
tetramethyl thiuram disulfide (thiuram);
n-dodecylguanidine acetate (dodine);
5 manganese ethylenebisdithiocarbamate (maneb);
1,4-dichloro-2,5-dimethoxybenzene (chloroneb);
methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate
(benomyl);
N-trichloromethylthiotetrahydrophthalimide (captan);
10 N-trichloromethylthiophthalimide (folpet);

Bactericides:

tribasic copper sulfate;
streptomycin sulfate;

Acaricides:

- 15 senecioic acid, ester with 2-sec-butyl-4,6-dinitrophenol
(Morocide®);
6-methyl-1,3-dithiolo[4,5-b]quinoxalin-2-one (Morestan®);
ethyl 4,4'-dichlorobenzilate (Folbex®);
1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane
20 (Kelthane®);
bis(pentachloro-2,4-cyclopentadien-1yl) (Pentac®);
tricyclohexyl tinhydroxide (cyhexatin);

Nematicides:

- S-methyl 1-(dimethylcarbamoyl)-N-(methylcarbamoyloxy)-
25 thioformimide (oxamyl);
S-methyl 1-carbamoyl-N-(methylcarbamoyloxy)thiofor-
mimide;
N-isopropylphosphoramidic acid, O-ethyl-O'-[4-(methyl-
thio)-m-tolyl]diester (fenamiphos);

30 Insecticides:

- methylcarbamic acid, ester with 2,3-dihydro-2,2-di-
methyl-7-benzofuranol (Furadan®);
O-[2,4,5-trichloro- α -(chloromethyl)benzyl]phosphoric
acid, O',O'-dimethyl ester (tetrachlorvinphos);
35 O-ethyl-O-(4-nitrophenyl)phenylphosphonothioate (EPN);
octachlorocamphene (toxaphene);

- cyano(3-phenoxyphenyl)methyl-4-chloro-alpha-(1-methylethyl)benzeneacetate (PydrinTM);
 (3-phenoxyphenyl)methyl(+)-cis,trans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
 5 (Ambush®);
 3-phenoxybenzyl-dl-cis,trans-chrysanthemate (phenothrin);
 2-mercaptosuccinic acid, diethyl ester, S-ester with
 thionophosphoric acid, dimethyl ester (malathion);
 phosphorothioic acid, O,O-dimethyl, O-p-nitrophenyl
 10 ester (methyl parathion);
 methylcarbamic acid, ester with α-naphthol (carbaryl);
 methyl N-(methylaminocarbonyloxy)ethaneimidothioate
 (methomyl);
 N'-(4-chloro-o-tolyl)-N,N-dimethylformamidine
 15 (chlordimeform);
 O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidylphosphorothioate (Diazinon®);
 O,S-dimethylacetylphosphoramidothioate (acephate);
 O,S-dimethylphosphoramidothioate (methamidophos).

20 Example 15

The foliage only of red kidney bean plants in the two-leaf stage was sprayed to run-off with aqueous dispersions of dimethyl N,N'-[[1,2-ethanediylbis(thio(methylimino)carbonyloxy)]]bis(ethanimidothioate) (I)
 25 at the dilutions indicated. The sprays contained Duponol L-144-WDG (sulfonated oleyl acetate surfactant) at a concentration of 1:3000. After drying, a single leaf from each treated plant was excised and placed in a covered 20 x 100 mm Petri dish containing a
 30 moistened filter paper and 10 southern armyworm (SAW) larvae approximately 13 mm in length. The test was conducted in duplicate. Insect mortality was evaluated two days later and is recorded below.

<u>Treatment</u>	<u>Concentration (% AI)</u>	<u>% Mortality SAW 2 Days</u>
I	0.01	100
	0.005	100
5	0.0025	75
untreated control	-----	0

Example 16

The plants from the test described in Example 10 were kept in a growth room at $77 \pm 2^\circ\text{F}$ and $53 \pm 5\%$ relative humidity for 7 days. At the end of that period of time the remaining cotyledonary leaf from each bean plant was placed singly in a Petri dish with southern armyworms as previously described. Insect mortality was again read 2 days later and is set forth below.

<u>Treatment</u>	<u>Concentration (% AI)</u>	<u>% Mortality SAW 2 Days</u>
I	0.01	100
	0.005	95
20	0.0025	50
untreated control	-----	0

Example 17

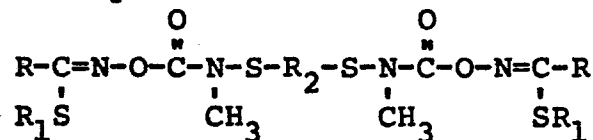
Cotton plants approximately 22 cm in height having 3-4 true leaves were sprayed to run-off with an aqueous dispersion of dimethyl N,N'-[[1,2-ethanediy]bis[thio(methylimino)carbonyloxy]]bis(ethanimidothioate) (I) at a concentration of 0.05%. The spray contained Duponol L-144-WDG at a concentration of 1:3000. Another set of plants was similarly treated with methomyl. Plant injury was evaluated 6 days after treatment and is recorded below.

<u>Treatment</u>	<u>Injury Rating *</u>
I	slight trace
35 methomyl	3

*Scale: 0 = no injury
10 = plant killed

CLAIMS:

1. A compound of the formula



wherein

- 5 R is branched or straight chain alkyl containing 1 to 3 carbon atoms or methoxymethyl;

R₁ is branched or straight chain alkyl containing 1 to 3 carbon atoms;

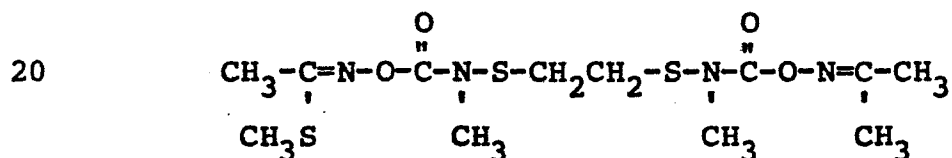
- 10 R₂ is -CH₂CH₂-, -CH₂ $\overset{\text{CH}_3}{\underset{|}{\text{CH}}}$ - or -CH₂CH₂ZCH₂CH₂-; and
Z is O or S.

2. The compound of claim 1 wherein R is methyl or ethyl and R₁ is methyl.

3. The compound of claim 1 or 2 wherein R is methyl and R₂ is -CH₂CH₂-.

- 15 4. The compound of claim 1 wherein R₂ is -CH₂CH₂- or -CH₂ $\overset{\text{CH}_3}{\underset{|}{\text{CH}}}$ -.

5. Dimethyl-N,N'-[[1,2-ethanediylbis[thio(methyl-imino)carbonyloxy]]]bis(ethanimidothioate) having the formula:



6. A composition suitable for control of pestiferous insects comprising an effective amount of an insecticidal compound and at least one of (a) an inert diluent and (b) a surfactant characterised in

5 that said insecticidal compound is a compound of any of claims 1-4.

7. The composition of claim 6 wherein said insecticidal compound is the compound of claim 5.

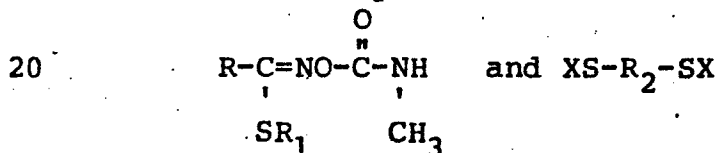
8. A method for control of pestiferous insects by applying to a locus of infestation, to the area to be protected or to the pests themselves, an effective amount of an insecticidal compound characterised in

that said insecticidal compound is a compound of any of claims 1-4.

9. The method of claim 8 wherein said insecticidal compound is the compound of claim 5.

10. A process for preparing a compound of claim 1 characterised in

that compounds of the formulae:



wherein

X is a halogen atom; and

R, R₁ and R₂ are as defined in claim 1, are reacted in an inert organic solvent in the presence
25 of a base.



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>US - A - 3 856 972 (FUJIMOTO...)</u> * First claim * /	1	C 07 C 153/00 A 01 N 9/12
			TECHNICAL FIELDS SEARCHED (Int.Cl. ²)
			C 07 C 153/00
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
☒ The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 17-08-1978	Examiner GAUTIER