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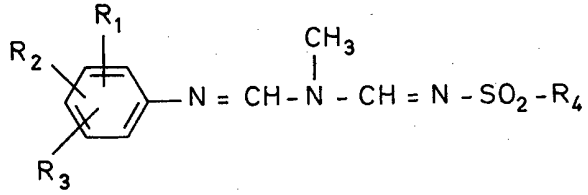
(19)

(54) N-ALKYLSULPHONYL-1,3,5-TRIAZAPENTA-1,4-DIENES, THEIR PREPARATION AND USE AS PESTICIDES

(71) We, CIBA-GEIGY AG, a Swiss body corporate, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to 1,3,5-triazapenta-1,4-dienes, their preparation and their use in pest control.

The 1,3,5-triazapenta-1,4-dienes have the formula



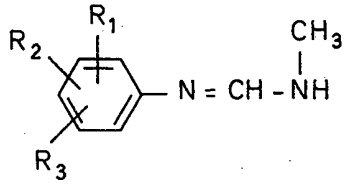
(I)

wherein each of R_1, R_2 and R_3, which may be the same or different, represents hydrogen, halogen, C_1—C_4alkyl, C_1—C_4alkoxy, trifluoromethyl or cyano, and R_4 represents C_1—C_4alkyl which is unsubstituted or substituted by halogen.

By halogen is meant fluorine, chlorine, bromine or iodine, in particular chlorine or bromine. The alkyl or alkoxy groups represented by R_1 to R_4 can be straight-chain or branched. Examples of such groups include: methyl, methoxy, ethyl, ethoxy, propyl, propoxy, n-butyl, n-butoxy, isobutyl, sec-butyl, tert-butyl.

Preferred compounds on account of their action are those of the formula I in which each of R_1, R_2 and R_3 represents, which may be the same or different, hydrogen, chlorine, bromine, methyl, trifluoromethyl, methoxy or cyano, and R_4 represents methyl or chloromethyl.

The compounds of the formula I can be obtained by methods which are known per se, for example by reacting a compound of the formula



wherein R_1, R_2 and R_3 are as defined in formula I, with a compound of the formula

$$RO—CH=N—SO_2R_4$$

in which R_4 is as defined in formula I and R represents C_1—C_4alkyl.

The process is generally carried out at a temperature between 0° and 120°C,

preferably between 40° and 100°C, under normal or elevated pressure and optionally in a solvent or diluent. Examples of suitable solvents or diluents are: ethers and ethereal compounds, such as diethyl ether, dipropyl ether, dioxane, dimethoxyethane and tetrahydrofurane; amides, such as N,N-dialkylated carboxamides; aliphatic, aromatic and halogenated hydrocarbons, in particular benzene, toluene, xylene, chloroform and chlorobenzene; nitriles, such as acetonitrile; dimethyl sulphoxide; ketones, such as acetone and methyl ethyl ketone.

The starting materials of the formulae II and III are known or they can be prepared by methods analogous to known ones.

The compounds of the formula I are suitable for combating animal and plant pests. The invention thus provides a method of combating animal or plants pests which method comprises applying to the pests or their locus a compound of the formula I. In particular, the compounds of the formula I have an outstanding action against insects and representatives of the order Acarina. They are therefore suitable for example for controlling mites and ticks of the species Tetranychus and Panonychus and of the families Dermanyssidae and Ixodidae as well as for controlling insects for example of the families: Tettigoniidae, Gryllidae, Gryllotalpidae, Blattidae, Reduviidae, Pyrrhocoridae, Cimicidae, Delphacidae, Aphididae, Diaspididae, Pseudococcidae, Scarabaeidae, Dermestidae, Coccinellidae, Tenebrionidae, Chrysomelidae, Bruchidae, Tineidae, Noctuidae, Lymantriidae, Pyralidae, Culicidae, Tipulidae, Stomoxydae, Trypetidae, Muscidae, Calliphoridae and Pulicidae.

In particular, the compounds of the formula I are suitable for controlling insects which are harmful to plants, especially insects which damage plants by eating, in ornamentals and crops of useful plants, especially in cotton plantations (e.g. Spodoptera littoralis and Heliothis virescens) and in vegetable crops (for example Leptinotarsa decemlineata and Myzus persicae).

The active compounds of the formula I also have a very good action against flies, for example Musca domestica and mosquito larvae.

The insecticidal and/or acaricidal action can be substantially broadened and adapted to prevailing circumstances by addition of other insecticides and/or acaricides. Examples of suitable additives include: organic phosphorus compounds, nitrophenols and derivatives thereof, formamidines, ureas, pyethroids, carbamates, and chlorinated hydrocarbons.

Compounds of the formula I are also combined with particular advantage with substances which exert a potentiating effect. Examples of such compounds include: piperonyl butoxide, propynyl ether, propynyl oximes, propynyl carbamates and propynyl phosphonates, 2-(3,4-methylenedioxyphenoxy)-3,6,9-trioxaundecane, S,S,S-tributylphosphorotrithioate.

The compounds of the formula I may be used as pure active substance or together with suitable carriers and/or other additives. Suitable carriers and additives can be solid or liquid and correspond to the substances conventionally used in the art of formulation, for example natural or regenerated substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders and/or fertilisers.

Solid pesticidal compositions according to the invention may contain, as active ingredient, a compound of the formula I together with a solid extender and, optionally a surface active agent and liquid pesticidal compositions may contain the active ingredient together with a liquid solvent and a surface active agent.

For application, the compounds of the formula I may be processed to dusts, emulsifiable concentrates, granules, dispersions, sprays, to solutions, or suspensions, in the conventional formulation which is commonly employed in application technology. In addition, cattle dips and spray races, in which aqueous preparations are used, may also be mentioned.

The compositions of the present invention may be prepared in known manner e.g. by homogeneously mixing and/or grinding active substances of the formula I with the suitable carriers, with or without the addition of dispersants or solvents which are inert to the active substances.

The compounds of the formula I may be processed to the following formulations:

Solid formulations:

Dusts, tracking powders and granules (coated granules, impregnated granules and homogeneous granules).

Liquid formulations:

A) water-dispersible active substance concentrates: wettable powders, pastes and emulsions;

b) solutions.

The content of active substance in the above described compositions is suitably between 0.1% and 95%.

The compounds (active substances) of the formula I can, for example, be formulated as follows (throughout the present specification all parts and percentages are by weight):

Dusts

The following substances are used to manufacture a) a 5% and b) a 2% dust:

a) 5 parts of active substance,
95 parts of talc;

b) parts of active substance,
1 part of highly disperse silicic acid,
97 parts of talc.

The active substances are mixed with the carriers and ground.

Granules

The following substances are used to produce 5% granules:

5 parts of active substance,
0.25 parts of epichlorohydrin,
0.25 parts of cetyl polyglycol ether,
3.50 parts of polyethylene glycol,
91 parts of kaolin (particle size 0.3—0.8 mm).

The active substance is mixed with epichlorohydrin and the mixture is dissolved in 6 parts of acetone; the polyethylene glycol and cetyl polyglycol ether are then added. The resultant solution is sprayed on kaolin, and the acetone is subsequently evaporated in vacuo.

Wettable powders:

The following constituents are used for the preparation of a) a 40%, b) and c) a 25%, and d) a 10% wettable powder:

a) 40 parts of active substance,
5 parts of sodium ligninsulphonate,
1 part of sodium dibutylnaphthalenesulphonate,
54 parts of silicic acid.

b) 25 parts of active substance,
4.5 parts of calcium ligninsulphonate,
1.9 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1),
1.5 parts of sodium dibutylnaphthalenesulphonate,
19.5 parts of silicic acid,
19.5 parts of Champagne chalk,
28.1 parts of kaolin,

c) 25 parts of active substance,
2.5 parts of isooctylphenoxy-polyoxyethylene-ethanol,
1.7 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1),
8.3 parts of sodium aluminium silicate,
16.5 parts of kieselguhr,
46 parts of kaolin;

d) 10 parts of active substance,
3 parts of a mixture of the sodium salts of saturated fatty alcohol sulphates,
5 parts of naphthalenesulphonic acid/formaldehyde condensate,
82 parts of kaolin.

The active substances are homogeneously mixed with the additives in suitable mixers and the mixture is then ground in appropriate mills and rollers. Wettable powders are obtained which can be diluted with water to give suspensions of the desired concentration.

Emulsifiable concentrates:

The following substances are used to produce a) a 10%, b) a 25%, and c) a 50% emulsifiable concentrate:

a) 10 parts of active substance,
3.4 parts of epoxidised vegetable oil,
3.4 parts of a combination emulsifier consisting of fatty alcohol polyglycol ether and alkylarylsulphonate calcium salt,
40 parts of dimethyl formamide,
43.2 parts of xylene;
b) 25 parts of active substance,
2.5 parts of epoxidised vegetable oil,
10 parts of alkylarylsulphonate/fatty alcohol polyglycol ether mixture,
5 parts of dimethyl formamide,
57.5 parts of xylene;
c) 50 parts of active substance,
4.2 parts of tributylphenol-polyglycol ether,
5.8 parts of calcium dodecylbenzenesulphonate,
20 parts of cyclohexanene,
20 parts of xylene.

By diluting these concentrates with water it is possible to obtain emulsions of the required concentration.

Sprays:

The following ingredients are used to prepare a) a 5% spray, and b) a 95% spray:

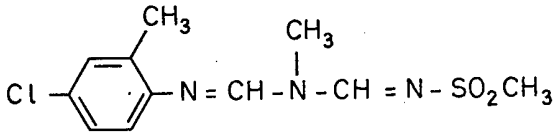
a) 5 parts of active substance,
1 part of epichlorohydrin,
94 parts of ligroin (boiling range 160°—190°C);
b) 95 parts of active substance,
5 parts of epichlorohydrin.

The invention is further illustrated by the following Examples.

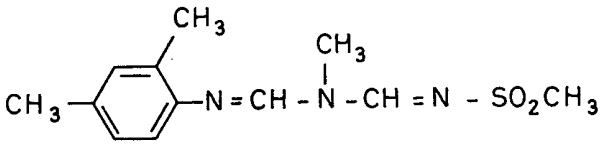
Example 1

Preparation of N-(2-methyl-4-chlorophenyl)-N′-methyl-N″-methylsulphonyl-1,3,5-triazapenta-1,4-diene

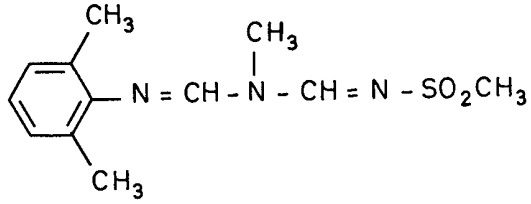
To a solution of 18.2 g of N-(2-methyl-4-chlorophenyl)-N′-methylformamidine in 60 ml of abs. dioxane are added dropwise at room temperature 15.1 g of N-ethoxymethylenemethanesulphonamide and the solution is stirred for 1 hour at 60°C. The reaction mixture is subsequently concentrated and the crystallised product is recrystallised from toluene, affording the compound of the formula



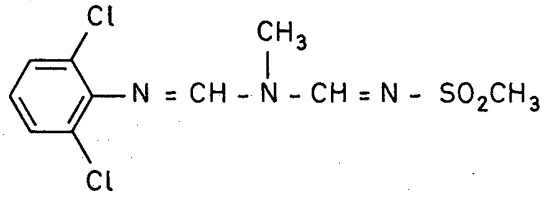
as a white powder with a melting point of 142°—143°C.
The following compounds are also prepared in analogous manner:



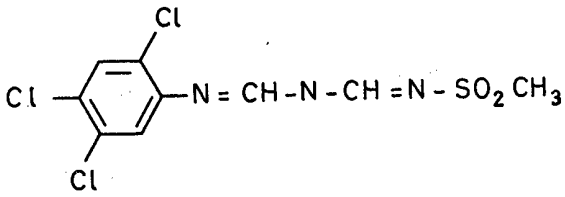
m.p.: 125—126°C



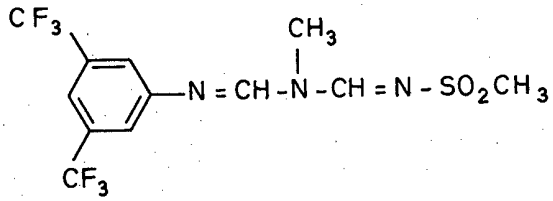
m.p.: 131—133°C



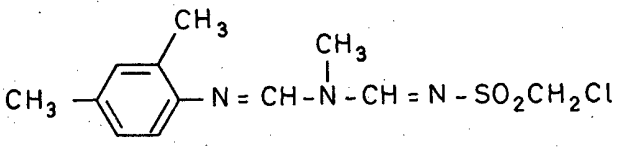
m.p.: 163—164°C



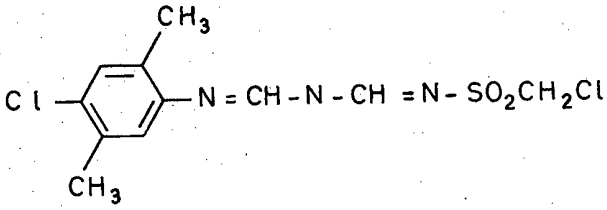
m.p.: 189—190°C



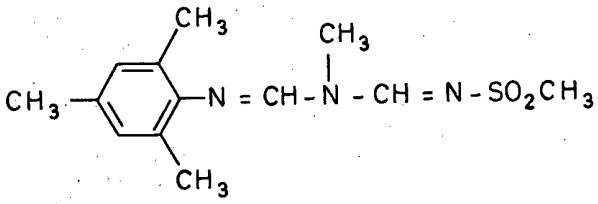
m.p.: 157—158°C



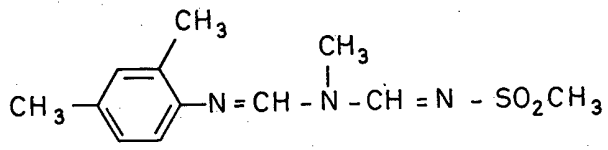
m.p.: 127—128°C



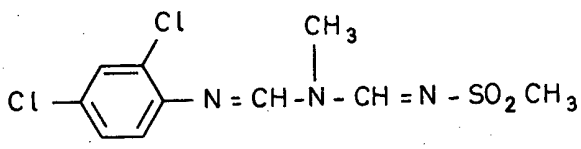
m.p.: 167—169°C



m.p.: 144—146°C



m.p.: 154—155°C



m.p.: 154—155°C

Example 2

A) Insecticidal stomach poison action

Cotton plants were sprayed with a 0.05% aqueous emulsion of active substance (obtained from a 10% emulsifiable concentrate). After the spray coating had dried, the cotton plants were populated with Spodoptera littoralis and Heliothis virescens in the L_3-stage. The test was carried out at 24°C and 60% relative humidity.

In this test, the compounds of Example 1 exhibited a good insecticidal stomach poison action against Spodoptera and Heliothis larvae.

B) Systemic insecticidal action

To determine the systemic action, bean plants (Vicia fabia) which had grown roots were put into a 0.01% aqueous solution of active substance (obtained from a 10% emulsifiable concentrate). Twenty four hours later, the parts of the plants above the soil were populated with aphids (Aphis fabae). By means of a special device the aphids were protected from any possible contact with the test substance either directly or via the gas phase. The test was carried out at 24°C and 70% relative humidity.

In this test, the compounds of Example 1 exhibited a systemic insecticidal action against Aphis fabae.

Example 3

Action against Chilo suppressalis

Rice seedings of the variety Caloro were transplanted into plastic pots (6 plants per pot) having a diameter of 17 cm at the top and reared to a height of about 60 cm. Infestation with Chilo suppressalis larve (L_1-stage, 3 to 4 mm in length) took place two days after the addition of active substance in granule form (rate of application: 8 kg of active ingredient per hectare) to the paddy water. Evaluation of the insecticidal action was made 10 days after addition of the granules. In this test, the compounds of Example 1 acted against Chilo suppressalis.

Example 4

Acaricidal action

Twelve hours before the test for acaricidal action, Phaseolus vulgaris plants were populated with an infested piece of leaf from a mass culture of Tetranychus urticae. The mobile stages which had migrated to the plants were sprayed with the emulsified test preparations from a chromatography atomiser in such a way that the spray broth did not run off. The number of living and dead larvae, adults and eggs was evaluated under a stereoscopic microscope after 2 to 7 days and the result expressed in percentage values. During the test run, the plants stood in greenhouse compartments at 25°C. In this test, the compounds of Example 1 acted against adults, larvae and eggs of Tetranychus urticae.

Example 5

Action on ticks

A) Rhipicephalus bursa

Five adult ticks and 50 tick larvae were counted into each of a number of test tubes and immersed for 1 to 2 minutes in 2 ml of an aqueous emulsion containing a concentration of 100, 10, 1 or 0.1 ppm of test substance. Each test tube was then sealed with a cotton-wool plug and placed on its head to enable the cotton wool to absorb the active substance emulsion.

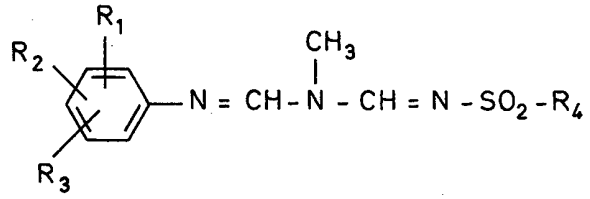
The adults were evaluated after 2 weeks and the larvae after 2 days. Each test was repeated twice.

B) Boophilus microplus (larvae)

Tests were carried out with 20 OP-sensitive and 20 OP-resistant larvae using aqueous emulsions similar to those used in Test A. (The resistance refers to the tolerance towards diazinone). The compounds of Example 1 acted in these tests against adults and larvae of Rhipicephalus bursa and OP-sensitive and OP-resistant larvae of Boophilus microplus.

WHAT WE CLAIM IS:—

1. A 1,3,5-triazapenta-1,4-diene of the formula



(I)

wherein

each of R_1, R_2 and R_3, which may be the same or different, represents a hydrogen, or halogen atom, or a C_1—C_4 alkyl, C_1—C_4 alkoxy, trifluoromethyl or cyano group, and

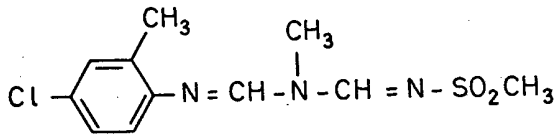
R_4 represents a C_1—C_4 alkyl group which is unsubstituted or substituted by halogen.

2. A 1,3,5-triazapenta-1,4-diene according to claim 1 wherein

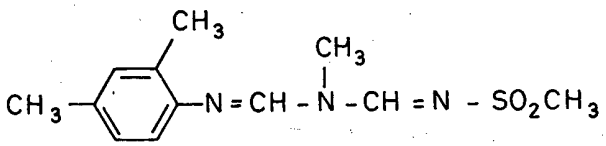
each of R_1, R_2 and R_3, which may be the same or different, represents a hydrogen, chlorine or bromine atom or a methyl, trifluoromethyl, methoxy or cyano group, and

R_4 represents a methyl or chloromethyl group.

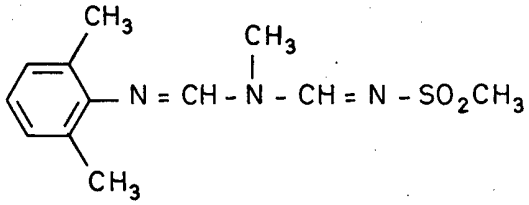
3. The 1,3,5-triazapenta-1,4-diene of the formula



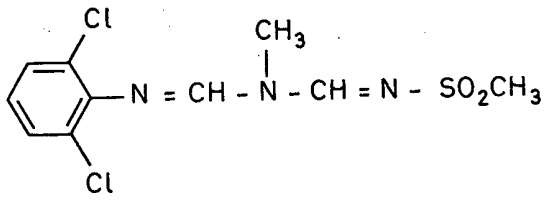
4. The 1,3,5-triazapenta-1,4-diene of the formula



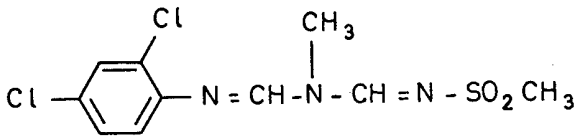
5. The 1,3,5-triazapenta-1,4-diene of the formula



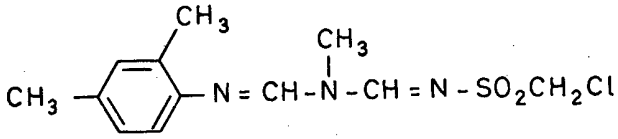
6. The 1,3,5-triazapenta-1,4-diene of the formula



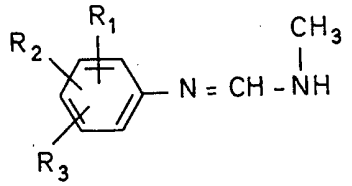
7. The 1,3,5-triazapenta-1,4-diene of the formula



8. The 1,3,5-triazapenta-1,4-diene of the formula



9. A process for preparing a 1,3,5-triazapenta-1,4-diene according to claim 1, which comprises reacting a compound of the formula



(wherein R_1, R_2 and R_3 are as defined in claim 1), with a compound of the formula

$$RO—CH=N—SO_2R_4$$

wherein R_4 is as defined in claim 1 and R represents a C_1—C_4 alkyl group.

10. A process for preparing a 1,3,5-triazapenta-1,4-diene according to claim 1 substantially as described with reference to Example 1.

11. A 1,3,5-triazapenta-1,4-diene according to claim 1 prepared by the process claimed in claim 9 or 10.

12. A pesticidal composition which contains, as active ingredient, a 1,3,5-triazapenta-1,4-diene according to any one of claims 1 to 6 and 8 together with a carrier and/or other additive.

13. A solid pesticidal composition which contains, as active ingredient, a 1,3,5-triazapenta-1,4-diene according to any one of claims 1 to 6 and 8 together with a solid extender and, optionally, a surface active agent.

14. A liquid pesticidal composition which contains, as active ingredient, a 1,3,5-triazapenta-1,4-diene according to any one of claims 1 to 6 and 8 together with a liquid diluent and a surface active agent.

15. A method of combating animal or plant pests which method comprises applying to the pests or their locus a 1,3,5-triazapenta-1,4-diene according to any one of claims 1 to 6 and 8.

16. A method according to claim 15 wherein the pests to be combated are insects or representatives of the order Acarina.

17. A pesticidal composition which contains, as active ingredient, a 1,3,5-triazapenta-1,4-diene according to claim 7 together with a carrier and/or other additive.

18. A solid pesticidal composition which contains, as active ingredient, a 1,3,5-triazapenta-1,4-diene according to claim 7 together with a solid extender and, optionally, a surface active agent.

19. A liquid pesticidal composition which contains, as active ingredient, a 1,3,5-triazapenta-1,4-diene according to claim 7 together with a liquid diluent and a surface active agent.

20. A method of combating animal or plant pests which method comprises applying to the pests or their locus a 1,3,5-triazapenta-1,4-diene according to claim 7.

21. A method according to claim 20 wherein the pests to be combated are insects or representatives of the order Acarina.

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