

1090.986



PATENT SPECIFICATION

NO DRAWINGS

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Inventors: CYRIL DONNINGER, JOHN HUGH DAVIES
and ROYSTON HENRY DAVIS

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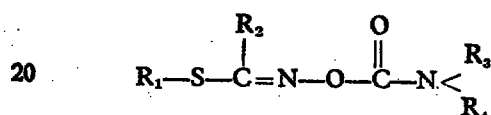
COMPLETE SPECIFICATION

Sulphur-Containing Oxime Carbamates

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V. a company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, 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:—

This invention relates to novel oxime carbamate derivatives, processes for their preparation and compositions containing them. The oxime carbamate derivatives are extremely useful in that they possess high biocidal activity, particularly insecticidal and nematocidal activity.

The novel compounds according to the invention may be represented by the following general formula:—



wherein R_1 represents a substituted or unsubstituted hydrocarbyl group; R_2 represents a substituted or unsubstituted hydrocarbyl group, or a nitrile group; and R_3 and R_4 each represent a hydrogen atom, or a substituted or unsubstituted alkyl or aryl group.

The hydrocarbyl group which R_1 and R_2 represent may be saturated or unsaturated and of aliphatic, cycloaliphatic, aromatic or of mixed type, e.g. aromatic substituted aliphatic group, such as benzyl, or an aliphatic substituted aromatic group. R_1 preferably represents an alkyl group having from 1—7 carbon atoms, an alkenyl group, or a phenyl group. R_2 preferably represents an alkyl group having from 1—7 carbon atoms or an alkenyl group.

Preferred compounds of the invention include:—

[Price 4s. 6d.]

- 1 - Methylthio - acetaldoxime N - methyl carbamate 40
- 1 - Ethylthio - acetaldoxime N - methyl carbamate
- 1 - Isopropylthio - acetaldoxime N - methyl carbamate 45
- 1 - Methylthiopropionaldoxime N - methyl carbamate
- 1 - Ethylthiopropionaldoxime N - methyl carbamate
- 1 - Allylthio - acetaldoxime N - methyl carbamate 50

These novel oxime carbamate derivatives may be prepared by reacting the appropriate 1 - hydrocarbylthio - aldoxime with the appropriate isocyanate, preferably in the presence of a base, e.g. a trialkylamine. The reaction is preferably carried out in an inert liquid reaction medium, e.g. methylene chloride or benzene.

Alternatively, the oxime carbamate derivatives may be prepared by the reaction of the appropriate 1 - hydrocarbylthio - aldoxime with phosgene and an amine or ammonia. This may conveniently be carried out by reacting an aqueous solution of a salt, conveniently an alkali metal salt, of the appropriate 1 - hydrocarbylthio - aldoxime with a solution of phosgene in a suitable solvent and further reacting with ammonia, or a primary or secondary amine to give the desired oxime carbamate derivative.

The appropriate 1 - hydrocarbylthio - aldoxime may be prepared by a process which comprises reacting the appropriate 1 - halo - oxime with a salt, conveniently an alkali metal salt, of the appropriate mercaptan in an organic reaction medium, e.g. methanol.

Alternatively, the appropriate 1 - hydrocarbylthio - aldoxime may be prepared by reacting the appropriate 1 - halo - oxime with a solution of sodium hydrogen sulphide and reacting the product with an appropriate

compound having a replaceable halogen atom, e.g. an alkyl halo acetate. This reaction is preferably carried out in a liquid medium.

- 5 A further process for the preparation of 1 - hydrocarbylthio - aldoximes comprises reacting the appropriate nitrile with the appropriate mercaptan in the presence of hydrogen chloride and reacting the product with a
10 hydroxy ammonium salt and a base, e.g. sodium acetate, to give the appropriate 1 - hydrocarbylthio - aldoxime.

- Both the 1 - hydrocarbylthio - aldoximes and the oxime carbamate derivatives, forming
15 part of the invention, may exist in two stereoisomeric forms, and this invention includes each isomeric form or a mixture thereof.

- The insecticidal activity of the compounds according to the invention has been demonstrated against a wide range of insects, including one or more of the following:—
20 flies, mosquito larvae, beetles, moth larvae, aphids and mites.

- The nematocidal activity of the compounds according to the invention has been demonstrated against nematodes e.g. (*Meloidogynae incognita*).

- The compounds of the invention, when used as biocides, may be applied in admixture with an inert diluent which may contain
30 a surface active agent. The invention also relates therefore, to biocidal compositions which comprise compounds of the invention and a carrier or a surface active agent, or
35 both a carrier and a surface active agent. The carrier may be a solid, a liquid or a compressed gas.

- The surface active agent may be anionic, cationic or nonionic and may take the form
40 of an emulsion, wetting agent or dispersing agent.

The compositions of the invention may be

Analysis

- 85 Found : C 24.4; H 6.8; N 13.3; S 30.4%
C₃H₇ONS requires : C 34.27; H 6.71; N 13.37; S 30.49%

- (b) 1 - Methylthio - acetaldoxime (10 w) was dissolved in dry methylene chloride (15.0 v). Triethylamine (two drops) and methyl isocyanate (0.8 w) were added and after the
90 initial reaction had subsided, the mixture was heated under reflux for ½ hour. After cooling the solvent was removed from the reaction mixture under reduced pressure and the pro-

formulated as a wettable powder, a dust, granules, a concentrate, a solution, an emulsifiable concentrate, a conventional emulsion, an
45 invert emulsion, an aerosol, or an encapsulated material.

The novel compounds of the invention may also be used in combination with each other or with other substances, for example, stabilisers, fertilisers and/or other biologically
50 active materials.

The invention also contemplates a method of combating insects and nematodes which comprises applying to said insects or nematodes or their habitat a compound of the
55 invention or a composition containing it.

The novel compounds, processes for their preparation, and their biocidal activity are further illustrated in the Examples that follow, in which parts by weight (w) and parts
60 by volume (v) bear the same relation as the kilograms to the litre.

EXAMPLE I

Preparation of 1 - methylthio - acet-
aldoxime N - methyl carbamate 65

- (a) A solution of 1 - chloroacetaldoxime (17 w) in methanol was added, drop by drop and with continuous stirring, to a solution of the sodium salt of methyl mercaptan (18 w) in
70 methanol. After completion of the addition, the mixture was heated under reflux for ½ hour. It was then cooled and filtered. The solvent was removed by evaporation under reduced pressure and the solid product
75 obtained was purified by chromatography on a silica-gel column using chloroform as eluant. The novel compound 1 - methylthio - acetaldoxime obtained in this manner was
80 further purified by recrystallisation from a mixture of benzene and petroleum ether to give 1 - methylthio - acetaldoxime. M.p. 92°C.

duct obtained purified by chromatography on a silica-gel column using a mixture of methylene chloride and diethyl ether (1:1) as eluant solvent. Recrystallisation from a mixture of benzene and petroleum ether gave 1 - methylthio - acetaldoxime N - methyl carbamate.
95 M.p. 77—77.5°C. 100

Analysis

- Found : C 37.2; H 6.2; N 17.3; S 19.9%
C₅H₁₀O₂N₂S requires : C 37.09; H 6.22; N 17.28; S 19.76%

EXAMPLE II
Preparation of 1-ethylthio - acet-
aldoxime N - methyl carbamate

(a) 1 - Ethylthio - acetaldoxime was pre-

pared according to the process described in
Example I(a) using the sodium salt of ethyl
mercaptan. M.p. 107—108°C.

Analysis

Found : C 40.5; H 7.4; N 11.9; S 26.8%
C₄H₉ONS requires : C 40.31; H 7.61; N 11.75; S 26.90%

(b) 1 - Ethylthio - acetaldoxime N - methyl
carbamate was prepared according to the pro-

cess described in Example I(b). M.p. 57—
58°C.

Analysis

Found : C 41.2; H 6.8; N 15.8; S 17.9%
C₆H₁₂O₂N₂S requires : C 40.91; H 6.82; N 15.92; S 18.18%

EXAMPLE III
Preparation of 1-isopropylthio - acet-
aldoxime N - methyl carbamate

(a) 1 - Isopropylthio - acetaldoxime was pre-

pared according to the process described in
Example I(a) using the sodium salt of iso-
propyl mercaptan.

Analysis

Found : C 45.2; H 8.2; N 10.7; S 24.1%
C₅H₁₁ONS requires : C 45.11; H 8.27; N 10.52; S 24.05%

(b) 1 - Isopropylthio - acetaldoxime N -
methyl carbamate was prepared according to

the process described in Example I(b). M.p. 30
60.5—61.5°C.

Analysis

Found : C 44.1; H 7.4; N 14.5; S 17.1%
C₇H₁₄O₂N₂S requires : C 44.21; H 7.37; N 14.73; S 16.84%

EXAMPLE IV
Preparation of 1-tert-butylthio - acet-
aldoxime N - methyl carbamate

(a) 1 - Tert-butylthio - acetaldoxime was

prepared according to the process described
in Example I(a) using the sodium salt of 40
tert-butyl mercaptan.

Analysis

Found : C 49.2; H 8.7; N 9.4; S 22.5%
C₈H₁₅ONS requires : C 48.96; H 8.9; N 9.52; S 22.7%

(b) 1 - Tert-butylthio - acetaldoxime N -
methyl carbamate was prepared according to

the process described in Example I(b), and
obtained as a viscous oil.

Analysis

Found : C 47.1; H 7.5; N 13.6; S 15.7%
C₈H₁₆O₂N₂S requires : C 47.04; H 7.90; N 13.72; S 15.69%

EXAMPLE V
Preparation of 1-tert-amylthio - acet-
aldoxime N - methyl carbamate

(a) 1 - Tert-amylthio - acetaldoxime was

prepared according to the process described
in Example I(a) using the sodium salt of tert-
amyl mercaptan, and was obtained as a vis-
cous oil.

Analysis

Found : C 52.1; H 9.0; N 8.7; S 19.6%
C₇H₁₅ONS requires : C 52.2; H 9.3; N 8.7; S 19.9%

(b) 1 - Tert - amylthio - acetaldoxime N - methyl carbamate was prepared according to the process described in Example I(b) and was obtained as a viscous oil.

5

Analysis

Found : C 49.4; H 8.1; N 12.6; S 14.9%
 $C_9H_{18}O_2N_2S$ requires : C 49.53; H 8.26; N 12.89; S 14.68%

EXAMPLE VI

Preparation of 1 - phenylthio - acetaldoxime N - methyl carbamate

pared according to the process described in Example I(a) using the sodium salt of benzenethiol.

10

(a) 1 - Phenylthio - acetaldoxime was pre-

15

Analysis

Found : C 57.4; H 5.5; N 8.3; S 19.5%
 C_9H_9ONS requires : C 57.48; H 5.43; N 8.38; S 19.18%

(b) 1 - Phenylthio - acetaldoxime N - methyl carbamate was prepared according to the process described in Example I(b). M.p. 121—122°C. 20

Analysis

Found : C 53.4; H 5.4; N 12.4; S 14.5%
 $C_9H_{13}N_2O_2S$ requires : C 53.54; H 5.4; N 12.49; S 14.29%

25

EXAMPLE VII

Preparation of 1 - methylthio - propionaldoxime N - methyl carbamate

67—68°C) was prepared according to the process described in Example I(a) using 1 - chloro - propionaldoxime. 30

(a) 1 - Methylthio - propionaldoxime (m.p.

Analysis

Found : C 40.2; H 7.6; N 11.6; S 27.0%
 C_4H_9ONS requires : C 40.33; H 7.56; N 11.77; S 26.89%

35

(b) 1 - Methylthio - propionaldoxime N - methyl carbamate was prepared according to the process described in Example I(b). M.p. 44°C.

Analysis

40

Found : C 40.9; H 6.5; N 15.9; S 18.1%
 $C_6H_{12}N_2O_2S$ requires : C 40.91; H 6.82; N 15.92; S 18.19%

(c) 1 - Methylthio - propionaldoxime (119 w) was dissolved in a solution containing sodium hydroxide (4 w) in water (150 v). This solution was added dropwise to a vigorously stirred solution of phosgene (19.8 w) in dichloromethane (100 v). The reaction temperature was maintained between 0—5°C by external cooling. When the addition was complete, the organic and aqueous layers were separated and the organic layer containing the oxime chloroformate was returned to the reaction vessel. Aqueous methylamine (25% w/v, 35 v) was added dropwise to the solution of chloroformate, vigorously stirred at -5°C to +5°C. The organic layer was separated, dried and evaporated under reduced pressure, leaving 1 - methylthio - propionaldoxime N - methyl carbamate as an oil which solidified on standing. The material was purified by silica gel/chloroform chromatography. M.p. 44°C. The infrared spectrum of this compound was determined and found to be the same as that prepared by the process described in Example VII(b). 60 65

50

separated and the organic layer containing the oxime chloroformate was returned to the reaction vessel. Aqueous methylamine (25% w/v, 35 v) was added dropwise to the solution of chloroformate, vigorously stirred at -5°C to +5°C. The organic layer was separated, dried and evaporated under reduced pressure, leaving 1 - methylthio - pro-

EXAMPLE VIII

Preparation of 1 - ethylthio - propionaldoxime N - methyl carbamate

(a) 1 - Ethylthio - propionaldoxime was prepared according to the process described in Example I(a) using 1 - chloro - propionaldoxime and the sodium salt of ethyl mercaptan. M.p. 48.5—49°C. 70

Analysis

Found : C 45.1; H 8.2; N 10.4; S 24.1%
 $C_5H_{11}ONS$ requires : C 45.11; H 8.27; N 10.52; S 24.05%

- (b) 1 - Ethylthio - propionaldoxime N - methyl carbamate was prepared according to the process described in Example I(b). M.p. 56.5—57.5°C.

Analysis

Found : C 44.5; H 7.7; N 14.4; S 16.5%
 $C_7H_{14}N_2O_2S$ requires : C 44.21; H 7.37; N 14.73; S 16.84%

EXAMPLE IX

Preparation of 1 - tert - butylthio - propionaldoxime N - methyl carbamate

- (a) 1 - Tert - butylthio - propionaldoxime was prepared according to the process de-

scribed in Example I(a) using 1 - chloro - propionaldoxime and the sodium salt of tert - butyl mercaptan and was obtained as a viscous oil.

Analysis

Found : C 52.0; H 9.0; N 8.3; S 19.7%
 $C_7H_{15}ONS$ requires : C 52.18; H 9.32; N 8.70; S 19.87%

- (b) 1 - Tert - butylthio - propionaldoxime N - methyl carbamate was prepared according to the process described in Example I(b), and obtained as a viscous oil.

Analysis

Found : C 49.5; H 8.2; N 12.5; S 14.9%
 $C_9H_{19}N_2O_2S$ requires : C 49.53; H 8.26; N 12.84; S 14.68%

EXAMPLE X

Preparation of 1 - n - heptylthio - propionaldoxime N - methyl carbamate

- (a) 1 - n - Heptylthio - propionaldoxime

was prepared according to the process described in Example I(a) using 1 - chloro - propionaldoxime and the sodium salt of n - heptyl mercaptan. M.p. 48—49°C.

Analysis

Found : C 59.4; H 10.1; N 6.9; S 16.1%
 $C_{10}H_{21}ONS$ requires : C 59.12; H 10.35; N 6.90; S 15.76%

- (b) 1 - n - Heptylthio - propionaldoxime N - methyl carbamate was prepared according to the process described in Example I(b). M.p. 32—33°C.

Analysis

Found : C 55.1; H 9.0; N 10.9; S 12.4%
 $C_{12}H_{25}O_2N_2S$ requires : C 55.39; H 9.23; N 10.76; S 12.30%

EXAMPLE IX

Preparation of 1 - methylthio - isobutyraldoxime N - methyl carbamate

- (a) 1 - Methylthio - isobutyraldoxime was

prepared according to the process described in Example I(a) using 1 - chloro - isobutyraldoxime. M.p. 64°C.

Analysis

Found : C 45.2; H 8.5; N 10.5; S 24.1%
 $C_5H_{11}ONS$ requires : C 45.11; H 8.27; N 10.52; S 24.05%

- (b) 1 - Methylthio - isobutyraldoxime N - methyl carbamate was prepared according to the process described in Example I(b) and obtained as a viscous oil.

Analysis

Found : C 43.7; H 7.5; N 14.2; S 16.5%
 $C_7H_{14}N_2O_2S$ requires : C 44.21; H 7.37; N 14.73; S 16.84%

EXAMPLE XII

- 5 Preparation of 1-methylthio-propionaldoxime N-3,4-dichlorophenyl carbamate

A sample of 1-methylthio-propionaldoxime, prepared as described in Example

I(a) using 1-chloro-propionaldoxime, was reacted with 3,4-dichlorophenyl-isocyanate under the conditions described in Example I(b). 1-Methylthio-propionaldoxime N-3,4-dichlorophenyl carbamate was obtained. M.p. 79—80°C.

10

15

Analysis

Found : C 42.9; H 3.9; N 8.8; Cl 22.1; S 10.3%
 $C_{11}H_{12}Cl_2N_2O_2S$ requires : C 43.0; H 3.91; N 9.12; Cl 23.15; S 10.4%

EXAMPLE XIII

- 20 Preparation of 1-tert-butylthio-1-cyano-formaldoxime N-methyl carbamate

Tert-butyl mercaptan (5.5 w) was added to a solution of sodium (1.4 w) in methanol.

- 25 A solution of monochloroglyoxime (7.8 w) dissolved in a minimum amount of methanol

was added dropwise to the stirred solution of sodium tert-butyl mercaptide. The temperature rose to 40°C. Stirring was continued at 40°C for a further hour. The solution was allowed to cool and the precipitate was filtered off, washed with water, and recrystallised from ethanol to give tert-butylthioglyoxime. M.p. 159°C.

30

35

Analysis

Found : C 41.4; H 6.5; S 18.2%
 $C_6H_{12}N_2SO_2$ requires : C 39.97; H 6.80; S 18.18%

- 40 Tert-butylthioglyoxime (3.2 w) was dissolved in dry dioxan (100 v). Triethylamine (two drops) and methyl isocyanate (2.8 w) were added. The reaction mixture was maintained at 25—30°C for 1 hour, then evaporated under reduced pressure. After removal of solvent, the residue was warmed until the evolution of gases had ceased, to give 1-

tert-butylthio-1-cyano-formaldoxime N-methyl carbamate as an oil which gave the following absorptions in the infrared spectrum:—

$\nu C=N = 2230\text{ cm}^{-1}$
 $\nu C=O = 1740\text{ cm}^{-1}$
 $\nu C-NH = 3320-3340\text{ cm}^{-1}$

50

Analysis

- 55 Found : C 45.0; H 6.4; N 14.4; S 18.9%
 $C_6H_{12}N_2SO_2$ requires : C 44.66; H 6.05; N 14.88; S 19.5%

EXAMPLE XIV

Preparation of 1-methylthio-1-cyano-formaldoxime N-methyl carbamate

60

The 1-methylthio-1-cyano-formaldoxime N-methyl carbamate was prepared according to the process described in Example XIII.

Analysis

- 65 Found : C 34.8; H 4.0; N 23.9; S 18.8%
 $C_5H_7N_3SO_2$ requires : C 34.68; H 4.5; N 24.28; S 18.4%

EXAMPLE XV
Preparation of 1-methylthio-but-3-enaldoxime

5 Methyl mercaptan (66 v) was added to a stirred solution of allyl cyanide (60.3 w) in equal volumes of light petroleum and ether (200 v). Hydrogen chloride was then passed into the reaction mixture maintained at 0°C for 4 hours. The solvent was decanted from the solid product and this product was washed with light petroleum. The product was then stirred with ether (300 v) and hydroxy ammonium chloride (62.7 w) in water (100 v). Sodium acetate (73.8 w) in

water (100 v) was immediately added and the reaction mixture was stirred at room temperature for 1 hour. Sodium carbonate was added until the pH was 4—5 and the ether layer was separated. The aqueous layer was extracted several times with ether and the combined ether extracts were dried and evaporated. The residue was chromatographed on silica gel using dichloromethane containing increasing proportions of ether as eluant to give both geometric isomers of 1-methylthiobut-3-enaldoxime. The isomer m.p. 29—30°C was eluted first and the isomer m.p. 49—50°C afterwards.

Analysis

30 Found m.p. 29—30°C : C 45.5; H 6.9; N 11.0; S 24.5%
m.p. 49—50°C : C 45.9; H 6.8; N 10.9; S 24.2%
C₅H₉NOS requires : C 45.81; H 6.87; N 10.69; S 24.42%

EXAMPLE XVI
Preparation of 1-ethoxycarbonylmethylthio-acetaldoxime

35 A solution of 1-chloro-acetaldoxime (25 w) in ether (100 v) was added dropwise with stirring to a solution obtained by dissolving sodium (10 w) and hydrogen sulphide (15 w) in methanol (300 v). When addition was complete, a solution of sodium (23 w) in methanol was added in one portion and the reaction mixture evaporated to dryness under reduced pressure. The resulting yellow

powder was suspended in benzene (250 v) and ethyl bromoacetate (35 v) added to the vigorously stirred suspension. When the addition was complete, the reaction mixture was refluxed and stirred for 15 minutes then filtered hot. The solid residue was extracted twice with hot benzene (250 v) and the combined extracts and filtrate evaporated to 250 v, then heated to redissolve the precipitated material and put to one side. On cooling, 1-ethoxycarbonylmethylthio-acetaldoxime crystallised. M.p. 90—91°C.

Analysis

Found : C 40.05; H 6.1; N 7.5; S 18.5%
C₈H₉O₂NS requires : C 40.66; N 6.26; N 7.9; S 18.3%

60 The melting point and analysis figures for certain 1-carbohydrothio-aldoximes and their carbamate derivatives, prepared by methods similar to those described in the preceding Examples, are set out in Table 1.
65 In this Table, column 2 refers by number to the particular Example whose procedure was followed to derive the indicated compound.

EXAMPLE XVII

70 Insecticidal activity of the oxime carbamate derivatives

75 A 0.1% by weight solution of active ingredient in an acetone/emulsifier mixture was prepared and taken up in a micrometer syringe. Adult female house flies (*Musca domestica*) were anaesthetised with carbon dioxide and 1 microlitre of the solution was

applied to the ventral abdomen of each fly. The treated flies were then placed in glass jars, each containing a small quantity of sugar as food for the flies. Twenty-four hours later the number of dead and moribund flies was recorded.

In addition to *Musca domestica*, six other species were included in the test. These were *Aedes aegypti* (mosquito larvae), *Phaedon cochleariae* (mustard beetles), *Plutella maculipennis* (diamond-back moth larvae), *Pieris brassica* (cabbage white butterfly), *Acyrtosiphon pisum* (pea aphids) and *Tetranychus telarius* (red spider mites). The test comprised exposure to aqueous dispersions for mosquito larvae, and exposure to sprayed foliage for mustard beetles, diamond-back moth larvae, pea aphids and red spider mites. The results are shown in Table 2.

TABLE 1

Compound	Method of preparation	Melting point °C	Analysis
1-methylthio-4-methylbenzaldoxime	I	72.5-73.5	Found : C 59.1; H 6.1; N 8.0; S 18.1% NSOC ₉ H ₁₁ requires : C 59.68; H 6.08; N 7.73; S 17.68%
1-methylthio-4-methylbenzaldoxime N-methyl carbamate	I	86.5-88	Found : C 55.6; H 5.7; N 12.1; S 13.5% N ₂ SO ₂ C ₁₁ H ₁₄ requires : C 55.46; H 5.88; N 11.77; S 13.45%
1-methylthio-4-chlorobenzaldoxime	I	77-79	Found : C 47.2; H 3.8; N 7.2; S 16.1; Cl 17.7% NSOClC ₈ H ₈ requires : C 47.64; H 3.97; N 6.95; S 15.88; Cl 17.62%
1-methylthio-4-chlorobenzaldoxime N-methyl carbamate	I	125-126	Found : C 46.7; H 4.6; Cl 13.8; S 12.1% N ₂ SO ₂ ClC ₁₀ H ₁₁ requires : C 46.41; H 5.24; Cl 13.73; S 12.38%
1-methylthio-propionaldoxime N-ethyl carbamate	I	20	Found : C 44.5; H 7.4; N 14.9; S 16.0% N ₂ SO ₂ C ₇ H ₁₄ requires : C 44.2; H 7.4; N 14.7; S 16.8%
1-ethylthio-propionaldoxime N-dimethyl carbamate	I	57-58	Found : C 47.2; H 7.60; N 13.8; S 15.8% N ₂ SO ₂ C ₈ H ₁₆ requires : C 47.08; H 7.84; N 13.73; S 15.68%
1-ethylthio-propionaldoxime N-phenyl carbamate	I	76-77	Found C 56.9; H 6.5; N 11.6; S 13.20% N ₂ SO ₂ C ₁₂ H ₁₆ requires : C 57.15; H 6.35; N 11.11; S 12.70%
1-(2,2-dichloroethyl)thio-propionaldoxime	I	61.5-62	Found : C 30.1; H 4.7; S 15.7; Cl 35.2% NSOCl ₂ C ₆ H ₉ requires : C 29.7; H 4.45; S 15.84; Cl 35.15%
1-(2,2-dichloroethyl) thio-propionaldoxime N-methyl carbamate	I	99-100	Found : C 33.1; H 4.9; S 12.8; Cl 27.2% N ₂ SO ₂ Cl ₂ C ₇ H ₁₂ requires : C 32.4; H 4.6; S 12.4; Cl 27.4%
1-(2-methoxyphenyl)thio-propionaldoxime	I	130-131	Found : C 56.7; H 6.2; N 6.8; S 15.0% NSO ₂ C ₁₀ H ₁₃ requires : C 56.87; H 6.16; N 6.63; S 15.17%
1-(2-methoxyphenyl)thio-propionaldoxime N-methyl carbamate	I	78-79	Found : C 53.2; H 5.9; N 10.8; S 11.8% N ₂ SO ₂ C ₁₂ H ₁₀ requires : C 53.74; N 5.97; N 10.45; S 11.94%

TABLE I continued

Compound	Method of preparation	Melting point °C	Analysis
1-(4-tert-butylphenyl)thio-propionaldoxime	I	145	Found : C 65.6; H 7.9; N 6.0; S 13.5% NSOC ₁₃ H ₁₉ requires : C 65.67; H 8.02; N 5.91; S 13.5%
1-(4-tert-butylphenyl)thio-propionaldoxime N-methyl carbamate	I	182-184	Found : C 61.4; H 7.6; N 9.7; S 11.1% N ₂ SO ₂ C ₁₅ H ₂₂ requires : C 61.24; H 7.48; N 9.53; S 10.88%
1-(4-chlorophenyl)thio-propionaldoxime	I	148.5-150	Found : C 50.2; H 4.8; S 14.6; N 6.2; Cl 16.6% NSOC ₆ H ₁₀ requires : C 50.12; H 4.64; S 14.52; N 6.5; Cl 16.47%
1-(4-chlorophenyl)thio-propionaldoxime N-methyl carbamate	I	112.5	Found : C 48.8; H 4.5; Cl 13.2; N 9.7; S 11.5% N ₂ SO ₂ ClC ₁₁ H ₁₃ requires : C 48.44; H 4.76; Cl 13.02; N 10.28; S 11.74%
1-(2-hydroxyethyl)thio-propionaldoxime	I	81-82.5	Found : C 40.7; H 7.1; N 9.2; S 21.0% NSO ₂ C ₆ H ₁₁ requires : C 40.3; H 7.38; N 9.4; S 21.47%
1-(2-hydroxyethyl)thio-propionaldoxime N-methyl carbamate	I	oil	Found : C 40.5; H 6.5; N 13.5; S 14.7% N ₂ SO ₂ C ₇ H ₁₄ requires : C 40.78; H 6.8; N 13.59; S 15.5%
1-(2-methylcarbamyloxyethyl)-thio-propionaldoxime N-methyl carbamate	I	76-78	Found : C 41.4; H 6.5; N 15.7; S 12.3% N ₂ SO ₂ C ₉ H ₁₇ requires : C 41.1; H 6.5; N 15.97; S 12.2%
1-ethoxycarbonyl-1-methylthio-formaldoxime	I	525-53.5	Found : C 36.7; H 5.5; N 8.5; S 19.6% NSO ₂ C ₆ H ₉ requires : C 36.81; H 5.52; N 8.59; S 18.63%
1-ethoxycarbonyl-1-methylthio-formaldoxime N-methyl carbamate	I	51-52	Found : C 39.7; H 5.4; N 12.8; S 14.6% N ₂ SO ₂ C ₇ H ₁₂ requires : C 38.19; H 5.45; N 12.73; S 14.54%
1-(2-acetoxyethyl)thio-propionaldoxime N-methyl carbamate	I	48-49	Found : C 43.4; H 6.4; N 11.4; S 13.0% N ₂ SO ₂ C ₉ H ₁₆ requires : C 43.54; H 6.45; N 11.29; S 12.9%

TABLE I continued

Compound	Method of preparation	Melting point °C	Analysis
1-allylthio-acetaldoxime	I	70-72	Found : C 46.1; H 6.7; N 10.2% NSOC ₅ H ₉ requires : C 45.8; H 6.87; N 10.69%
1-allylthio-acetaldoxime N-methyl carbamate	I	56-58	Found : C 44.3; H 6.0; N 14.7; S 17.0% N ₂ SO ₂ C ₇ H ₁₁ requires : C 44.68; H 6.38; N 14.89; S 17.02%
1-allylthio-propionaldoxime N-methyl carbamate	I	64-65.5	Found : C 47.2; H 7.1; S 15.9; N 13.3% N ₂ SO ₂ C ₈ H ₁₄ requires : C 47.52; H 6.93; S 15.84; N 13.87%
1-cyanomethylthio-acetaldoxime N-methyl carbamate	XVI	100-101.5	Found : C 38.2; H 4.4; N 22.8; S 17.3% N ₂ SO ₂ C ₆ H ₉ requires : C 38.5; H 4.81; N 22.5; S 17.11%
1-ethoxycarbonylmethylthio-acetaldoxime N-methyl carbamate	XVI	oil	Found : C 41.0; H 5.9; N 12.2; S 13.7% N ₂ SO ₂ C ₈ H ₁₄ requires : C 41.01; H 6.02; N 11.96; S 13.68%
1-methylthio-but-3-enaldoxime N-methyl carbamate α isomer	I	oil	Found : C 44.6; H 6.4; N 15.1; S 17.30% N ₂ SO ₂ C ₇ H ₁₂ requires : C 44.68; H 6.38; N 14.89; S 17.02%
1-methylthio-but-3-enaldoxime N-methyl carbamate β isomer	I	oil	Found : C 44.6; H 6.5; N 14.6; S 17.2% N ₂ SO ₂ C ₇ H ₁₂ requires : C 44.68; H 6.38; N 14.89; S 17.02%

1-me
N-me1-eth
N-me1-isp
N-me1-ter
N-me1-ter
N-me1-me
N-me1-eth
N-me1-tert
doxin1-n-h
aldox1-me
N-me1-me
doxin1-ally
N-me1-tert-
maldo
carbar

TABLE 2

Compound	Musca domestica	Aedes aegypti	Phaedon cochleariae	Plutella maculipennis	Pieris brassica	Acrythosiphon pisum	Tetranychus telarius
1-methylthio-acetaldoxime N-methyl carbamate	A	B	B	A	A	A	A
1-ethylthio-acetaldoxime N-methyl carbamate	A	A	A	A	A	A	A
1-isopropylthio-acetaldoxime N-methyl carbamate	A	A	A	A	A	A	A
1-tert-butylthio-acetaldoxime N-methyl carbamate	A	A	B	A	A	A	A
1-tert-amylthio-acetaldoxime N-methyl carbamate	A	A	A	A	A	A	A
1-methylthio-propionaldoxime N-methyl carbamate	A	A	B	A	A	A	A
1-ethylthio-propionaldoxime N-methyl carbamate	A	A	A	A	A	A	A
1-tert-butylthio-propionaldoxime N-methyl carbamate	A	A	A	A	A	A	A
1-n-heptylthio-propionaldoxime N-methyl carbamate	C	A	C	B	B	B	A
1-methylthio-butyraldoxime N-methyl carbamate	A	A	A	A	A	A	A
1-methylthio-but-3-enal-doxime N-methyl carbamate	A	A	B	B	A	A	A
1-allylthio-acetaldoxime N-methyl carbamate	A	A	B	A	A	A	A
1-tert-butylthio-1-cyano-formaldoxime N-methyl carbamate	A	C	C	A	A	A	A

A = 100% kill
 B = some kill
 C = no kill

EXAMPLE XVIII

Nematocidal activity of the oxime carbamate derivatives

- 5 An aqueous solution of the desired oxime carbamate derivative was mixed with a suspension of larvae of root knot nematode (*Meloidogyne incognita*) in a watch glass.

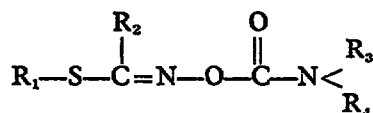
The watch glass was covered and incubated in the dark at 23°C for 24 hours. After incubation the watch glass was illuminated and 10 nematodes observed for movement under a microscope. The tests were carried out in duplicate and the figures in Table 3 represent the percentage of moving nematodes.

TABLE 3

Name of compound	Percentage mobility at concentrations expressed in parts per million		
	10	50	100
1-ethylthio-acetaldoxime N-methyl carbamate	40	10	0
1-methylthio-propionaldoxime N-methyl carbamate	50	0	0
1-isopropylthio-acetaldoxime N-methyl carbamate	40	40	0
1-methylthio-acetaldoxime-N-methyl carbamate	70	40	0
1-ethylthio-propionaldoxime N-methyl carbamate	70	40	0
Control	90	100	90

WHAT WE CLAIM IS:—

1. Compounds having the following general formula:—



- 20 wherein R_1 represents a substituted or unsubstituted hydrocarbyl group; R_2 represents a substituted or unsubstituted hydrocarbyl group or a nitrile group; and R_3 and R_4 each represent a hydrogen atom, or a substituted or unsubstituted alkyl or aryl group.

2. Compounds as claimed in claim 1 wherein R_1 represents an alkyl group having from 1—7 carbon atoms or an alkenyl group.

- 30 3. Compounds as claimed in claims 1 and 2 wherein R_1 represents a phenyl group.

4. Compounds as claimed in any one of the preceding claims wherein R_2 represents an alkyl group having from 1—7 carbon atoms.

- 35 5. Compounds as claimed in any one of the preceding claims wherein R_2 represents an alkenyl group.

6. 1 - Methylthio - acetaldoxime N - methyl carbamate.

- 40 7. 1 - Ethylthio - acetaldoxime N - methyl carbamate.

8. 1 - Isopropylthio - acetaldoxime N - methyl carbamate.

9. 1 - Methylthio - propionaldoxime N - methyl carbamate.

10. 1 - Ethylthio - propionaldoxime N - methyl carbamate.

11. 1 - Allylthio - acetaldoxime N - methyl carbamate.

12. A process for the preparation of compounds claimed in any one of claims 1—11 wherein the appropriate 1-hydrocarbylthio-aldoxime derivative is reacted with the appropriate isocyanate.

13. A process as claimed in the preceding claim wherein the reaction is carried out in the presence of a base.

14. A process for the preparation of compounds claimed in claims 1—11 wherein a solution of a salt of the appropriate 1-hydrocarbylthio-aldoxime derivative is reacted with a solution of phosgene in a suitable organic solvent and further reacting with ammonia or an appropriate primary or secondary amine.

15. A process for preparing the 1-hydrocarbylthio-aldoxime derivatives used as intermediates in the preparation of the oxime carbamates claimed in claims 1—11 which comprises reacting the appropriate 1-halo-oxime with a salt of the appropriate mercaptan in an organic reaction medium.

16. A process as claimed in the preceding claim in which the reaction medium is methanol.

17. A process for preparing the 1-hydrocarbylthio-aldoxime derivatives used as intermediates in the preparation of the oxime carbamates claimed in claims 1—11 which

EXAMPLE XVIII

Nematocidal activity of the oxime carbamate derivatives

- 5 An aqueous solution of the desired oxime carbamate derivative was mixed with a suspension of larvae of root knot nematode (*Meloidogyne incognita*) in a watch glass.

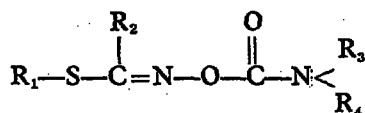
The watch glass was covered and incubated in the dark at 23°C for 24 hours. After incubation the watch glass was illuminated and 10 nematodes observed for movement under a microscope. The tests were carried out in duplicate and the figures in Table 3 represent the percentage of moving nematodes.

TABLE 3

Name of compound	Percentage mobility at concentrations expressed in parts per million		
	10	50	100
1-ethylthio-acetaldoxime N-methyl carbamate	40	10	0
1-methylthio-propionaldoxime N-methyl carbamate	50	0	0
1-isopropylthio-acetaldoxime N-methyl carbamate	40	40	0
1-methylthio-acetaldoxime N-methyl carbamate	70	40	0
1-ethylthio-propionaldoxime N-methyl carbamate	70	40	0
Control	90	100	90

WHAT WE CLAIM IS:—

1. Compounds having the following general formula:—



- 20 wherein R_1 represents a substituted or unsubstituted hydrocarbyl group; R_2 represents a substituted or unsubstituted hydrocarbyl group or a nitrile group; and R_3 and R_4 each represent a hydrogen atom, or a substituted or unsubstituted alkyl or aryl group.

- 25 2. Compounds as claimed in claim 1 wherein R_1 represents an alkyl group having from 1—7 carbon atoms or an alkenyl group.

- 30 3. Compounds as claimed in claims 1 and 2 wherein R_1 represents a phenyl group.

4. Compounds as claimed in any one of the preceding claims wherein R_2 represents an alkyl group having from 1—7 carbon atoms.

- 35 5. Compounds as claimed in any one of the preceding claims wherein R_2 represents an alkenyl group.

6. 1 - Methylthio - acetaldoxime N - methyl carbamate.

- 40 7. 1 - Ethylthio - acetaldoxime N - methyl carbamate.

8. 1 - Isopropylthio - acetaldoxime N - methyl carbamate.

9. 1 - Methylthio - propionaldoxime N - methyl carbamate.

10. 1 - Ethylthio - propionaldoxime N - methyl carbamate.

11. 1 - Allylthio - acetaldoxime N - methyl carbamate.

12. A process for the preparation of compounds claimed in any one of claims 1—11 wherein the appropriate 1 - hydrocarbylthio - aldoxime derivative is reacted with the appropriate isocyanate.

13. A process as claimed in the preceding claim wherein the reaction is carried out in the presence of a base.

14. A process for the preparation of compounds claimed in claims 1—11 wherein a solution of a salt of the appropriate 1 - hydrocarbylthio - aldoxime derivative is reacted with a solution of phosgene in a suitable organic solvent and further reacting with ammonia or an appropriate primary or secondary amine.

15. A process for preparing the 1 - hydrocarbylthio - aldoxime derivatives used as intermediates in the preparation of the oxime carbamates claimed in claims 1—11 which comprises reacting the appropriate 1 - halo-oxime with a salt of the appropriate mercaptan in an organic reaction medium.

16. A process as claimed in the preceding claim in which the reaction medium is methanol.

17. A process for preparing the 1 - hydrocarbylthio - aldoxime derivatives used as intermediates in the preparation of the oxime carbamates claimed in claims 1—11 which



- comprises reacting the appropriate 1-halo-oxime with a solution of sodium hydrogen sulphide and reacting the product with an appropriate compound having a replaceable halogen atom.
18. A process as claimed in the preceding claim wherein the compound having a replaceable halogen atom is an alkyl haloacetate.
19. A process for preparing the 1-hydrocarbylthio-aldoxime derivatives used as intermediates in the preparation of the oxime carbamates claimed in claims 1—11 which comprises reacting the appropriate nitrile with the appropriate mercaptan in the presence of hydrogen chloride and reacting the product obtained with a hydroxy ammonium salt and a base.
20. A process for the preparation of compounds specified in any one of claims 1—11 substantially as hereinbefore described.
21. A process substantially as hereinbefore described in any one of Examples I to XVI or in Table 1.
22. An insecticidal composition comprising a compound as specified in any one of claims 1—11 and a carrier or a surface active agent or both a carrier and a surface active agent.
23. A nematocidal composition comprising a compound as specified in any one of claims 1—11 and a carrier or a surface active agent or both a carrier and a surface active agent.
24. A composition as claimed in claims 22 and 23 formulated as a wettable powder, a dust, granules, a concentrate, a solution, an emulsifiable concentrate, a conventional emulsion, an invert emulsion or an encapsulated material.
25. A composition as claimed in any one of claims 22 to 24 substantially as hereinbefore described in Example XVII and XVIII.
26. Novel compounds as defined in claim 1 and methods for their preparation as hereinbefore described in Examples I to XVI and in Table 1.
27. Novel compounds as defined in claim 1 substantially as hereinbefore described.
28. A method of combating insects which comprises applying to said insects and/or their habitat a compound as claimed in any one of claims 1—11, 26 or 27 or a composition as claimed in any one of claims 22—25.
29. A method of combating nematodes which comprises applying to said nematodes and/or their habitat a compound as claimed in any one of claims 1—11, 26 or 27 or a composition as claimed in any one of claims 22—25.

WILLENS AND ROBBINS,
Chartered Patent Agents,
Shell Centre,
London, S.E.1.
Agents for the Applicants.

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