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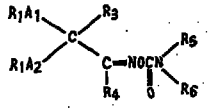
(54) S,S-SUBSTITUTED 2,2-THIO-, SULFINYL-, AND SULFONYL-ALKANYL AND -ALKANONE N-SUBSTITUTED CARBAMOYLOXIMES

(71) We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation of the State of Delaware, United States of America, of 3M Center, Saint Paul, Minnesota 55101, United States of America, 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:—

Certain alkanyl and alkanone oxime carbamates are known to the art which possess insecticidal, miticidal or nematocidal activity, for example see U.S. patents 3,299,137 and 3,217,037. However, compounds in which one alpha carbon atom of the alkanyl or alkanone portion of an oxime is bonded to two substituted sulphur atoms, or their respective carbamate derivatives, have not been previously reported nor has the use of the latter as effective insecticides, acaricides and nematocides been suggested.

This invention relates to S,S - substituted carbamoyloxide derivatives which possess insecticidal, acaricidal and nematocidal activity.

The present invention provides compounds of the formula



wherein A_1 and A_2 are independently selected from thio, sulfinyl and sulfonyl linkages, R_1 R_2 and R_3 are independently selected from alkyl and alkenyl radicals having up to 4 carbon atoms, or R_1 and R_2 when taken together comprise an alkylene or alkylene group having from 2 to 12 carbon atoms, 2 to 5 carbon atoms of which form a chain linking the sulfur atoms, R_4 is hydrogen or an alkyl radical having up to 4 carbon atoms, and R_5 and R_6 are independently selected from hydrogen, and alkyl, cycloaliphatic, alkoxy and alkenyl radicals having up to 10 carbon atoms, and only one of R_5 and R_6 may be hydrogen.

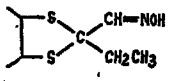
In the preferred compounds of the present invention R_3 is methyl or ethyl, R_1 and R_2 together either contain no more than 5 carbon atoms or form an alkylene linking group having 2 or 3 carbon atoms in the chain linking the sulfur atoms, R_4 is hydrogen, R_5 is methyl or ethyl and R_6 is hydrogen. Such compounds are preferred because they exhibit a superior degree of nematocidal activity although all of the compounds disclosed herein have a degree of nematocidal action.

As starting material for the preparation of the above compounds there may be employed oxime compounds which may be prepared from the corresponding aldehydes or ketones, for example an aldehyde of the formula

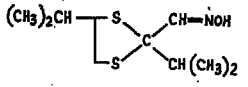
$$\begin{matrix} R_1A_1 \\ R_2A_2 \end{matrix} \!\!>\!C\!< \begin{matrix} CHO \\ R_3 \end{matrix}$$

by reaction with a strong acid salt of hydroxylamine e.g. hydroxylamine hydrochloride in water or an organic solvent e.g. ethanol, preferably in the presence of an acid acceptor such as potassium acetate, and at a temperature in the range 0 to 200° C.

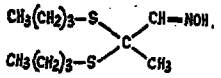
Some exemplary oximes are the following:



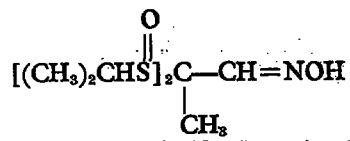
2 - formyl - 2 - ethyl - 4,5 - dimethyl - 1,3-dithiolane oxime



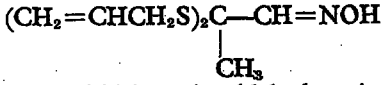
2 - formyl - 2,4 - diisopropyl - 1,3 - dithiolane oxime



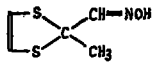
α,α - bis(n - butylthio)propionaldehyde oxime



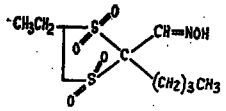
α,α - bis(isopropylsulfinyl)propionaldehyde oxime



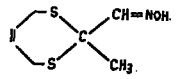
α,α - bis(allylthio)propionaldehyde oxime



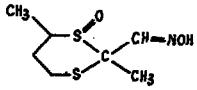
2 - formyl - 2 - methyl - 1,3 - dithiole oxime



2 - formyl - 2 - (*n* - butyl) - 4 - ethyl - 1,3-dithiolane oxime tetraoxide



5 - formyl - 5 - methyl - 4,6 - dithiepin oxime

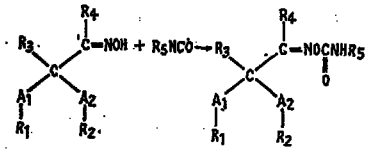


2 - formyl - 2,6 - dimethyl - 1,3 - dithiane oxime monoxide

The aldehyde and ketone precursors used to prepare useful starting material oximes may be prepared by formylation or alkanoylation of dithio - substituted carbon atoms in the presence of very strong bases, as described by E. J. Corey et al., Angewandte Chemie, International Edition, 4, 1075 (1965).

When the reaction of alpha - ketoaldehyde with mercaptans is applied to symmetrical alpha - diketones, only one isomeric ketomercaptol is possible. When this reaction is applied to unsymmetrical alpha-diketones, isomeric mixtures of ketomercaptols are obtained which must be separated.

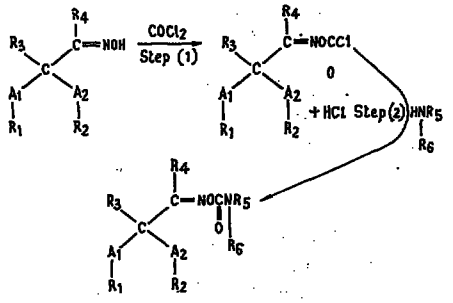
The carbamoyloxime compounds of this invention can be prepared in a variety of ways from the correspondingly substituted oximes. One synthetic route involves addition of an isocyanate to the substituted oxime having R_1, R_2, R_3 and R_4 substitutents corresponding to the desired compound and is illustrated by the following equation wherein A_1, A_2, R_1, R_2, R_3, R_4 and R_5 are defined as before:



The isocyanate addition can be carried out, generally, by contacting the oxime with the isocyanate in an inert organic solvent, and preferably in the presence of a tertiary amine as a catalyst. The reaction may be effected at temperatures ranging from 10° C. to 130° C. and is preferably carried out between room temperatures and 80° C. Generally, temperatures substantially in excess of 130° C. are to be avoided in view of the temperature sensitivity of the product carbamoyloxime. The operating pressure may range from 1 atmosphere to 10 atmospheres, preferably from 1 to 3 atmospheres, and is dependent upon the concentration and vapour pressure of the volatile isocyanate at the reaction temperature. The inert organic solvents that can be employed in the reaction are those inert to isocyanates in general, i.e. those free of radicals such as hydroxy or amino radicals. Illustrative solvents are aliphatic ketones such as acetone, aliphatic and aromatic hydrocarbons, such as hexane, heptane, octane, benzene, and toluene, and others such as diethyl ether, and ethyl propyl ether. Generally, amounts of said tertiary amine catalyst from 0.1 to 1.0 weight percent of the starting material comprised of an isocyanate and the oxime are sufficient. Aliphatic and/or aromatic tertiary amines are useful for this purpose, e.g. dimethylaniline, and triethylamine. The mole ratio of isocyanate to oxime can range from 0.25:1 to 2:1, but preferably an equimolar amount or slight excess of the isocyanate is employed to ensure that the oxime is completely reacted. The reaction time may vary from 5 minutes to 7 days, but normally when operating in the preferred temperature range, reaction times of from one-half hour to 5 hours are sufficient for complete reaction.

The carbamoyloxime product formed, either as a solid or as an oily liquid, can be recovered from the reaction mixture by means known to the art, e.g. by vacuum-distillation to drive off solvent and excess isocyanate.

Another synthetic route involves the reaction of a substituted oxime with phosgene to form the chloroformate which in turn is reacted with a compound containing a reactive amino (—NH) function such as a primary or secondary amine, or substituted hydroxylamine to give the desired oxime carbamate of this invention. The synthesis is illustrated by the following equations wherein A_1, A_2, R_1, R_2, R_3, R_4, R_5 and R_6 are defined as before:



In step (1) above, a solution of the oxime compound in e.g. ethyl ether is conveniently added slowly to a solution of phosgene in toluene or ethyl ether or other suitable organic solvent preferably in the presence of a hydrochloric acid acceptor such as a suitable amine, e.g. dimethyl aniline. The reaction can be carried out at from −30° C. to 40° C., but will generally be found to proceed most advantageously between −10° C. and room temperature. The reaction is slightly exothermic so that some external cooling is usually necessary to maintain the temperature within the desired range. The reaction mixture can be washed with water to remove the byproduct amine hydrochloride and the organic layer containing the chloroformate (IV) can be used for further reactions. The addition of the reactant containing a reactive amino function, step (2) above, is carried out in the presence of a solvent for said reactant, such as water, dioxane, toluene or chloroform, at a temperature between −40° C. and 80° C. and preferably below 40° C. Inasmuch as the reaction proceeds smoothly even at low temperatures and is so rapid above 40° C. that loss of low boiling reactants may occur and some decomposition may take place.

The sulfinyl- and sulfonyl-linked compounds of our invention can be prepared by oxidizing the corresponding sulfide-linked carbamoyloxime compound of the invention with dilute solutions of peracetic acid or with sodium metaperiodate. Alternatively, the oxidation step may be carried out using the alkanyl, alkanone or oxime intermediates, using selective conditions known to the art. It may be desirable, or even necessary, to protect the carbonyl group before oxidation, for example by forming the acetal or ketal.

The invention will be further understood by reference to the following illustrative and non-limiting examples, in which all parts are by weight unless otherwise noted. All melting points given are uncorrected.

Example 1

α,α - Bis(methylthio)propionaldehyde oxime N - methylcarbamate

N,N,N′,N′ - Tetramethylethylenediamine (11.6 g., 0.1 mole) is added to 71.5 ml. of 1.4 *N* n - butyllithium in hexane at −20° C. Acetaldehyde dimethyldithioacetal (12.2 g., 0.1 mole) is added dropwise to this mixture. After 2 hours, 8.05 g. of dimethylformamide (0.11 mole) is added dropwise. The reaction is allowed to warm to room temperature and stirred overnight. The mixture is poured into 200 ml. of water, acidified and extracted with 75 ml. of hexane three times. The combined extracts are washed with 100 ml. of 2 percent potassium hydroxide and 50 ml. of water two times, dried over magnesium sulfate and evaporated *in vacuo*. The residue weighs 9.95 g. The infrared spectrum of the product is consistent with the assigned structure for *α,α* - bis(methylthio)propionaldehyde.

α,α - Bis(methylthio)propionaldehyde (9.95 g., 55 mmoles), potassium acetate (6.47 g., 66 mmoles) and hydroxylamine hydrochloride (4.58 g., 66 mmoles) are refluxed for 3 hours in 80 ml. of ethanol. Potassium chloride is removed by filtration and the filtrate evaporated to near dryness. The addition of ice precipitates a cream coloured solid which is collected by filtration. The infrared spectrum is consistent with the assigned structure for *α,α* - bis(methylthio)propionaldehyde oxime.

Four drops of triethylamine and 3.8 g. of *α,α* - bis(methylthio)propionaldehyde oxime (23 mmoles) are dissolved in 30 ml. of chloroform. Methyl isocyanate (5.24 g., 92 mmoles) in 10 ml. of chloroform is added dropwise, with stirring. The mixture is heated to reflux, refluxed for two hours and then evaporated *in vacuo*. The residual oil is triturated with a 50/50 mixture of hexane and benzene. This solid is recrystallized from 50/50 hexane/benzene, and the product has a melting point of 62—65° C. Its infrared and proton magnetic resonance spectra are consistent with the assigned structure of the desired carbamoyloxime compound.

Anal. Calculated for $C_7H_{14}N_2O_2S_2$: C, 37.8; H, 6.3; N, 12.6
Found: C, 38.1; H, 6.1; N, 12.4.

Using the procedure of Example 1 the products of the following table are obtained using commercially available isocyanates as the reactants.

TABLE I

Ex. No.	Reactants: Oxime	Reactants: Isocyanate	Product
2	α,α-bis(methylthio)-propionaldehyde oxime	*n*-butyl isocyanate	α,α-bis(methylthio)-propionaldehyde oxime N-*n*-butylcarbamate
3	"	allyl isocyanate	α,α-bis(methylthio)-propionaldehyde oxime N-allylcarbamate
4	"	ethyl isocyanate	α,α-bis(methylthio)-propionaldehyde oxime N-ethylcarbamate
5	"	cyclohexyl isocyanate	α,α-bis(methylthio)-propionaldehyde oxime N-cyclohexylcarbamate

EXAMPLE 6

2 - Formyl - 2 - methyl - 1,3 - dithiolane oxime N,N - dimethylcarbamate

A stirred mixture of 360.3 g of a 40 percent aqueous solution of pyruvaldehyde (2.0 moles), 179 g. of 1,2 - ethanedithiol (1.90 moles), 600 ml. of benzene and 2.0 g. of *p* - toluenesulfonic acid hydrate is heated at reflux for 4 hours, during which time about 175 ml. of water separates in a Dean-Stark trap. The dark brown solution is stirred for 6 hours at room temperature, then poured into 300 ml. of diethyl ether. This solution is washed with 500 ml. of 5 percent sodium bicarbonate solution, then 500 ml. of water, and dried over magnesium sulfate. The dried solution is fractionally distilled under water pump vacuum, and the fraction boiling from 105 to 108° C. is examined by infrared analysis. The spectrum of the fraction is consistent for the structure of 2 - formyl - 2 - methyl - 1,3 - dithiolane.

Anal. Calculated for $C_5H_8OS_2$:
C, 40.5; H, 5.4
Found: C, 40.7; H, 5.6.

Using the general method described, the following derivatives of α - dicarbonyl compounds useful as intermediates for the preparation of oxime intermediates are prepared from known starting materials. These intermediates are identified by their method of synthesis and infrared spectro.

2 - formyl - 2 - methylcyclohexano - 1,3-dithiolane,
2 - formyl - 2,4,6 - trimethyl - 1,3 - dithiane
2 - formyl - 2 - methyl - 1,3 - dithiane,
2 - formyl - 2,4 - dimethyl - 1,3 - dithiolane,
2 - formyl - 2,5 - dimethylbenzo - 1,3-dithiolane,
2 - formyl - 2 - methyl - 4 - phenyl - 1,3-dithiolane,
2 - formyl - 2,4 - dimethyl - 1,3 - dithiane,
4 - ethyl - 2 - formyl - 2 - methyl - 1,3-dithiolane,
2 - acetyl - 2 - methyl - 1,3 - dithiolane,
2 - acetyl - 2,4 - dimethyl - 1,3 - dithiolane, and
2 - ethyl - 2 - propionyl - 1,3 - dithiolane.

A stirred mixture of 162.4 g. of 2 - formyl-2 - methyl - 1,3 - dithiolane (1.1 moles), 83.4 g. of hydroxylamine hydrochloride (1.2 moles), 117.8 g. of potassium acetate (1.2 moles) and 1:1 ethanol-water (1.0 liter) is heated at reflux for 6 hours, then cooled in a freezer overnight. White crystals of 2 - formyl - 2 - methyl - 1,3 - dithiolane oxime are collected by filtration, washed with a cold solution of 1:1 ethanol-water (200 ml.) and dried *in vacuo*, m.p. 104—106.5° C.

Anal. Calculated for $C_5H_9NOS_2$:
C, 36.8; H, 5.6; N, 8.6
Found: C, 37.0; H, 5.5; N, 8.3.

Using the general method described, the following oxime intermediates are prepared from the compounds described above in Example 6.

2 - formyl - 2 - methylcyclohexano - 1,3-dithiolane oxime,
2 - formyl - 2,4,6 - trimethyl - 1,3 - dithiane oxime,
2 - formyl - 2 - methyl - 1,3 - dithiane oxime,
2 - formyl - 2,4 - dimethyl - 1,3 - dithiolane oxime,

2 - formyl - 2,5 - dimethylbenzo - 1,3-dithiolane oxime,
2 - formyl - 2 - methyl - 4 - phenyl - 1,3-dithiolane oxime,
2 - formyl - 2,4 - dimethyl - 1,3 - dithiane oxime,
4 - ethyl - 2 - formyl - 2 - methyl - 1,3-dithiolane oxime,
2 - acetyl - 2 - methyl - 1,3 - dithiolane oxime,
2 - acetyl - 2,4 - dimethyl - 1,3 - dithiolane oxime, and
2 - ethyl - 2 - propionyl - 1,3 - dithiolane oxime.

To a stirred, cold (0—5° C.) solution of 24 g. of N,N - dimethylaniline (0.2 mole) and 200 ml. of diethyl ether under a nitrogen atmosphere and protected by a Dry Ice condenser is added by bubbling 22 g. of gaseous phosgene (0.22 mole). As the solution becomes cloudy, 32.6 g. of 2 - formyl - 2 - methyl-1,3-dithiolane oxime (0.20 mole) dissolved in 200 ml. of diethyl ether is added dropwise while maintaining the reaction temperature between −5 and +5° C. After the completion of the addition, the reaction is stirred for an additional hour at 0° C., then filtered. The colorless filtrate is reduced in volume to 240 ml.

To an 80 ml. portion of this filtrate maintained at 0—5° C. is added dropwise with stirring 9.0 g. of dimethylamine (0.20 mole). This solution is stirred for an additional hour at 0° C., and the white solid product removed by filtration. Recrystallization from *n*-hexane gives white crystals, m.p. 75—76° C. The infrared spectrum of the compounds is consistent with the structure of 2 - formyl - 2-methyl - 1,3 - dithiolane oxime N,N - dimethylcarbamate.

EXAMPLE 7

4 - Butyl - 2 - formyl - 2 - methyl - 1,3 - dithiolane oxime N,N - dimethylcarbamate

Using the procedure of Example 6 and replacing 2 - formyl - 2 - methyl - 1,3 - dithiolane with 4 - butyl - 2 - formyl - 2-methyl - 1,3 - dithiolane the desired product is obtained, as indicated by infrared spectral analysis, as white crystals when recrystallized from *n*-hexane.

EXAMPLE 8

2 - Formyl - 2 - methyl - 1,3 - dithiolane oxime N - methylcarbamate

To a stirred solution of 2 - formyl - 2-methyl 1,3 - dithiolane oxime (81.6 g., 0.50 mole), triethylamine (1.0 ml.) and acetone (50 ml.) is added 30.8 g. of methyl isocyanate (0.54 mole) in 50 ml. of acetone. This reaction mixture is heated at reflux temperature for 12 hours, cooled and filtered. The volume of the solution is reduced to about 250 ml. by evaporation under vacuum. The product is obtained as a white solid and recrystallized from acetone, m.p. 122—124° C. The infrared spectrum is consistent with the assigned structure.

Anal. Calculated for $C_7H_{12}N_2O_2S_2$:
C, 38.2; H, 5.5
Found: C, 38.0; H, 5.4.

Using the procedure of Example 8 the products of the following table are obtained using commercially available isocyanates as reactants. The oximes may be prepared as in Example 6.

TABLE II

Ex. No.	Reactants: Oxime	Reactants: Isocyanate	Product
9	2-formyl-2-methyl-1,3-dithiolane oxime	ethyl isocyanate	2-formyl-2-methyl-1,3-dithiolane oxime N-ethylcarbamate m.p. 122—125°C.
10	"	*n*-butyl isocyanate	2-formyl-2-methyl-1,3-dithiolane oxime N-*n*-butylcarbamate m.p. 67—70°C.
11	"	allyl isocyanate	2-formyl-2-methyl-1,3-dithiolane oxime N-allylcarbamate m.p. 53—54°C.
12	2-formyl-2-methyl-1,3-dithiane oxime m.p. 145—147.5°C.	methyl isocyanate	2-formyl-2-methyl-1,3-dithiane oxime N-m thylcarbamate m.p. 96—99°C.

TABLE II (Continued)

Ex. No.	Reactants: Oxime	Reactants: Isocyanate	Product
13	2-formyl-2,4-dimethyl-1,3-dithiolane oxime m.p. 63—65°C.	methyl isocyanate	2-formyl-2,4-dimethyl-1,3-dithiolane oxime N-methylcarbamate m.p. 73—76°C.
14	2-formyl-2,4,6-trimethyl-1,3-dithiane oxime	methyl isocyanate	2-formyl-2,4,6-trimethyl-1,3-dithiane oxime N-N-methylcarbamate m.p. 45—50°C.
15	2-formyl-2-methylcyclohexano-1,3-dithiolane oxime	methyl isocyanate	2-formyl-2-methylcyclohexano-1,3-dithiolane oxime N-methylcarbamate m.p. 132—134°C.
16	2-formyl-2-methyl-1,3-dithiolane oxime	*t*-butyl isocyanate	2-formyl-2-methyl-1,3-dithiolane oxime N-*t*-butylcarbamate m.p. 84—86°C.
17	2-formyl-2,5-dimethyl-benzo-1,3-dithiolane oxime	methyl isocyanate	2-formyl-2,5-dimethyl-N-methylcarbamate m.p. 125—127°C.
18	2-formyl-2-methyl-4-phenyl-1,3-dithiolane oxime	methyl isocyanate	2-formyl-2-methyl-4-phenyl-1,3-dithiolane oxime N-methylcarbamate m.p. 129—132°C.
19	2-formyl-2,4-dimethylyl-1,3-dithiane oxime	methyl isocyanate	2-formyl-2,4-dimethyl-1,3-dithiane oxime N-methylcarbamate m.p. 106—107°C.
20	4-ethyl-2-formyl-2-methyl-1,3-dithiolane oxime	methyl isocyanate	2-ethyl-2-formyl-2-methyl-1,3-dithiolane oxime N-methylcarbamate
21	2-acetyl-2-methyl-1,3-dithiolane oxime	methyl isocyanate	2-acetyl-2-methyl-1,3-dithiolane oxime N-methylcarbamate m.p. 107—109°C.
22	2-acetyl-2,4-dimethyl-1,3-dithiolane oxime	methyl isocyanate	2-acetyl-2,4-dimethyl-1,3-dithiolane oxime N-methylcarbamate m.p. 89—92°C.

EXAMPLE 23

2 - Formyl - 2 - methyl - 1,3 - dithiolane oxime N - methylcarbamate S,S' - bisdioxide

To a stirred, cold (0—5° C.) solution of 2-formyl - 2 - methyl - 1,3 - dithiolane oxime N-methylcarbamate (4.4 g., 0.02 mole) in glacial acetic acid (75 ml.) is added dropwise 30 percent hydrogen peroxide solution (18.1 g., 0.16 mole). The solution is then heated to reflux for 2.5 hours. Next, 75 ml. of water is added, and the solution is cooled slowly. White crystals separate and are collected by filtration, m.p. 155° C. (dec.). The infrared spectrum is consistent with the assigned structure.

EXAMPLE 24

2 - Formyl 2 - methyl - 1,3 - dithiolane oxime N - methylcarbamate S - oxide

To a cold (0.—5° C.) solution of 2 - formyl-2 - methyl - 1,3 - dithiolane oxime N - methylcarbamate (4.4 g., 0.02 mole) in methanol (100 ml.) is added sodium metaperiodate (4.3 g., 0.02 mole) in water (50 ml.). External cooling is necessary to maintain the temperature at 0—5° C. The mixture is stirred cold for 4 hours, then allowed to warm to room temperature, and the white solid is removed by filtration. The filtrate is reduced in volume *in vacuo* to afford an oil which slowly solidifies. Recrystallization from 1:1 ethyl acetate: benzene gives beige crystals, m.p. 96—97° C. (dec.). The infrared spectrum of this compound is consistent with the assigned structure.

EXAMPLE 25

2 - Formyl - 2 - methyl - 1,3 - dithiolane oxime N - methylcarbamate S,S' - dioxide

To a stirred, cold (0—5° C.) solution of 2-formyl - 2 - methyl - 1,3 - dithiolane oxime N-methylcarbamate (4.4 g., 20 mmole) in methanol (150 ml.) is added dropwise over fifteen minutes a solution of sodium metaperiodate (9.0 g., 42 mmoles) in water (100 ml.). A white precipitate forms. The mixture is stirred cold (5—10° C.) for 45 minutes and filtered. The filtrate is evaporated *in vacuo*, removing the solvent. The residue is extracted three times with chloroform (50 ml. portions), the extracts are dried over magnesium sulfate, and the chloroform removed *in vacuo*. Diethyl ether is added to the residue, then removed *in vacuo*. Chloroform and hexane are added to the residue and the mixture is heated. The product, 2 - formyl - 2 - methyl - 1,3 - dithiolane oxime N - methylcarbamate S,S' - dioxide, m.p. 126° C. (dec.), a tan solid, is removed by filtration. Cooling the filtrate gives a second crop of product.

Anal. Calculated for $C_7H_{13}N_2O_4S_2$:
C, 33.3; H, 4.8; N, 11.1
Found: C, 33.0; H, 4.8; N, 11.0.

The carbamoyloxime derivatives of the invention are tested for nematocidal activity by a standard test method using roots of tomato plants infested with nematodes (*Meloidogyne incognita*, var. acrita). They are tested for acaricidal activity by a standard test method using cotton plants infested with *Tetranychus telarium* and for their insecticidal activity using houseflies (*Musca domestica*) and mosquito larvae (*Aedes aegypti*).

The following compounds were found to have a particularly high degree of activity as nematocides, acaricides or insecticides:

2 - formyl - 2 - methyl - 1,3 - dithiolane oxime N - methylcarbamate,

2 - formyl - 2 - methyl - 1,3 - dithiane oxime N - methylcarbamate,

2 - formyl - 2,4 - dimethyl - 1,3 - dithiolane oxime N - methylcarbamate.

While all of the carbamyloxime compounds falling within the scope of the present invention as described in the general formula set forth hereinabove exhibit some nematicidal or insecticidal activity, it is to be understood that some are more effective than others. The above-listed compounds are examples of preferred embodiments which exhibit high activity, particularly as nematocides.

The compounds contemplated in this invention may be applied as insecticides, acaricides and nematocides according to methods known to those skilled in the art. Pesticidal compositions containing the compounds as the active toxicant will usually comprise a carrier or diluent, either liquid or solid.

Liquid concentrates may be prepared by dissolving one of these compounds with a solvent such as acetone or xylene and dispersing the toxicants in water with the aid of suitable surface active agent, i.e. dispersing and emulsifying agents.

The choice of dispersing and emulsifying agent and the amount employed is dictated by the nature of the composition and the ability of the agent of facilitate the dispersion of the toxicant. Generally, it is desirable to use as little of the agent as is possible, consistent with the desired dispersion of the toxicant in the spray so that rain does not re-emulsify the toxicant after it is applied to the plant and wash it off the plant. Nonionic, anionic or cationic surface active agents may be employed, for example, the condensation products of alkylene oxides with phenol and organic acids, alkyl aryl sulfonates, complex ether alcohols, and quaternary ammonium compounds.

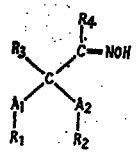
In the preparation of wettable powder or dust or granulated compositions, the active ingredient is dispersed in and on an appropriately divided solid carrier such as clay, talc, bentonite, diatomaceous earth, charcoal, corn cob granules, or fullers earth. In the formulation of the wettable powders the aforementioned surface active agents as well as lignosulfonates can be included.

The required amount of the toxicants contemplated herein may be applied per acre treated in from 1 to 200 gallons or more of water as diluent or in from 5 to 500 pounds of inert solid carrier or diluent. The concentration in the liquid concentrate will usually vary from 5 to 30 percent by weight, and in the solid formulations from 2 to 80 percent by weight. The formulations are applied in amounts which contain from one-fourth to 15 pounds of active toxicant per acre.

The pesticides contemplated herein prevent attack by insects, mites and nematodes upon plants or other material to which the pesticides are applied, and they have a high residual activity. With respect to plants they have a

high margin of safety in that when used in sufficient amount to kill or repel the insects, they do not burn or injure the plant. The toxicants are sufficiently chemically inert that they are compatible with substantially any other constituents of the spray schedule, and they may be used in the soil, upon the seeds or the roots of plants without injuring either the seeds or roots of plants, yet by imbibition or root uptake they may kill the pests feeding thereon. Furthermore, their properties are such that they are not unacceptably hazardous to the user.

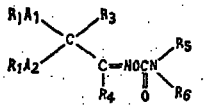
In our United Kingdom patent application No. 16013/72 (Serial No. 1286543) we have described and claimed an oxime having the formula



wherein A_1 and A_2 are independently selected from thio, sulfinyl and sulfonyl linkages, R_1, R_2 and R_3 are independently selected from alkyl and alkenyl radicals having up to 4 carbon atoms, or R_1 and R_2 when taken together form an alkylene or alkenylene group having from 2 to 12 carbon atoms, 2 to 5 carbon atoms of which form a chain linking the sulfur atoms and R_4 is hydrogen or alkyl radical having up to 4 carbon atoms, and methods for the preparation of such oxides.

WHAT WE CLAIM IS:—

1. A compound having the formula



wherein A_1 and A_2 are independently selected from thio, sulfinyl and sulfonyl linkages, R_1, R_2 and R_3 are independently selected from alkyl and alkenyl radicals having up to 4 carbon atoms, or R_1 and R_2 when taken together comprise an alkylene or alkenylene group having from 2 to 12 carbon atoms, 2 to 5 carbon atoms of which form a chain linking the sulfur atoms, R_4 is hydrogen or an alkyl radical having up to 4 carbon atoms, and R_5 and R_6 are independently selected from hydrogen, and alkyl, cycloaliphatic, alkoxy and alkenyl radicals having up to 10 carbon atoms, and only one of R_5 and R_6 may be hydrogen.

2. A compound according to claim 1 wherein A_1 and A_2 are —S—linking groups.

3. A compound according to claims 1 or 2 wherein R_1 and R_2 together form an alkylene or alkenylene linking group joining the sulphur atoms.

4. A compound according to any of claims 1 to 3 wherein R_4 is hydrogen, and R_1 and R_2 together contain no more than 5 carbon atoms.

5. α,α - bis(methylthio)propionaldehyde oxime N - methylcarbamate.

6. 2 - formyl - 2 - methyl - 1,3 - dithiolane oxime N - methylcarbamate.

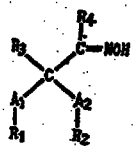
7. 2 - formyl - 2 - methyl - 1,3 - dithiane oxime N - methylcarbamate.

8. 2 - formyl - 2,4 - dimethyl - 1,3 - dithiolane oxime N - methylcarbamate.

9. 2 - acetyl - 2 - methyl - 1, 3- dithiolane oxime N - methylcarbamate.

10. 2 - acetyl - 2,4 - dimethyl - 1,3-dithiolane oxime N - methylcarbamate.

11. A process for producing S,S - substituted thio-, sulfinyl-, sulfonyl-alkanyl and -alkanone N - substituted carbomoyloximes which comprises contacting an oxime of the formula



with a substituted isocyanate of the formula

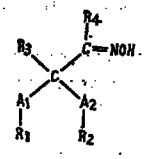
$$R_5—N=C=O$$

in an inert organic solvent, wherein A_1, A_2 and R_1 to R_5 have the significations described in claim 1.

12. A process according to claim 11, in which a tertiary amine is employed as a catalyst.

13. A process according to claim 11 or 12 wherein R_4 is hydrogen, and R_1 and R_2 together contain no more than 5 carbon atoms.

14. A process for producing S,S - substituted thio-, sulfinyl-, sulfonyl- alkanyl and -alkanone and N - substituted carbamoyloximes which comprises reacting an oxime of the formula



with phosgene, in an inert solvent solution, to form the chloroformate which in turn is reacted with a compound having the formula

$$\begin{matrix} HNR_5 \\ | \\ R_6 \end{matrix}$$

in an inert organic solvent at a temperature of from −40° C. to 80° C., wherein A_1, A_2, and R_1 to R_6 have the above mentioned significations.

high margin of safety in that when used in sufficient amount to kill or repel the insects, they do not burn or injure the plant. The toxicants are sufficiently chemically inert that they are compatible with substantially any other constituents of the spray schedule, and they may be used in the soil, upon the seeds or the roots of plants without injuring either the seeds or roots of plants, yet by imbibition or root uptake they may kill the pests feeding thereon. Furthermore, their properties are such that they are not unacceptably hazardous to the user.

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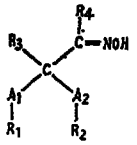

wherein A_1 and A_2 are independently selected from thio, sulfinyl and sulfonyl linkages, R_1, R_2 and R_3 are independently selected from alkyl and alkenyl radicals having up to 4 carbon atoms, or R_1 and R_2 when taken together form an alkylene or alkenylene group having from 2 to 12 carbon atoms, 2 to 5 carbon atoms of which form a chain linking the sulfur atoms and R_4 is hydrogen or alkyl radical having up to 4 carbon atoms, and methods for the preparation of such oxides.

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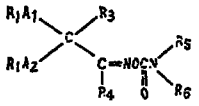

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3. A compound according to claims 1 or 2 wherein R_1 and R_2 together form an alkylene or alkenylene linking group joining the sulphur atoms.

4. A compound according to any of claims 1 to 3 wherein R_4 is hydrogen, and R_1 and R_2 together contain no more than 5 carbon atoms.

5. α,α - bis(methylthio)propionaldehyde oxime N - methylcarbamate.

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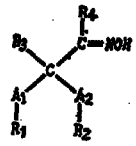

with a substituted isocyanate of the formula

$$R_5—N=C=O$$

in an inert organic solvent, wherein A_1, A_2 and R_1 to R_5 have the significations described in claim 1.

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13. A process according to claim 11 or 12 wherein R_4 is hydrogen, and R_1 and R_2 together contain no more than 5 carbon atoms.

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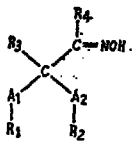

with phosgene, in an inert solvent solution, to form the chloroformate which in turn is reacted with a compound having the formula

$$\begin{array}{l} HNR_5 \\ | \\ R_6 \end{array}$$

in an inert organic solvent at a temperature of from −40° C. to 80° C., wherein A_1, A_2, and R_1 to R_6 have the above mentioned significations.

* C L M S *

15. A process according to claim 14 in which the compound containing the amino function is a primary or secondary amine.

16. A process according to claim 14 in which the compound containing the amino function is a substituted hydroxylamine.

17. A process according to claim 14, 15, or 16 in which R_4 is hydrogen, and R_1 and R_2 together contain no more than 5 carbon atoms.

18. A process according to any of claims 14 to 17 including the step of preparing the said oxime by contacting an aldehyde of the formula

$$\begin{matrix} R_1A_1 & & CHO \\ & >C< & \\ R_2A_2 & & R_3 \end{matrix}$$

with a strong acid salt of hydroxylamine in water or an organic solvent at a temperature in the range of 0 to 200° C. wherein A_1, A_2 and R_1 to R_3 have the afore-mentioned significations.

19. A process according to any of claims 14 to 18 wherein a hydrochloric acid acceptor is employed.

20. A process according to any of claims 14 to 19 in which A_1 and A_2 are S-linking groups.

21. A process according to any of claims 14 to 19 in which R_1 and R_2 together form an alkylene or alkenylene linking group joining the carbon atoms.

22. A process for preparing an S,S substituted thio-, sulfinyl-, or sulfonyl- alkanyl or -alkanone N - substituted carboyloxime substantially as described in any of Examples 1 to 5, 7 to 13, 23 and 24 herein or for preparing 2 - formyl - 2 - methyl - 1,3 - dithiolane oxime N,N - dimethylcarbamate, substantially as described in Example 6 herein.

23. A process for preparing an S,S substituted thio-, sulfinyl- or sulfonyl- alkanyl or -alkanone N - substituted carbamolyoxime other than 2 - formyl - 2 - methyl - 1,3 dithiolane oxime N,N - dimethylcarbamate substantially as described in Example 6 herein or substantially as described in any of Examples 14 to 22 or 25 herein.

24. A compound made by a process according to any of claims 13, 17 and 22.

25. A compound made by a process according to any of claims 11, 12 14 to 16, 18 to 21 and 23.

26. A method for preventing injury to plants by insects, acarids or nematodes which comprises applying to the plants, or to the soil in which they are growing, an effective amount of a compound according to any of claims 4 to 8 or 24.

27. A method for preventing injury to plants by insects, acarids or nematodes which comprises applying to the plants, or to the soil in which they are growing, an effective amount of a compound according to any of claims 1 to 3, 9 to 10 or 25.

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