

Patented Aug. 3, 1943

2,325,720

UNITED STATES PATENT OFFICE

2,325,720

PARASITICIDE

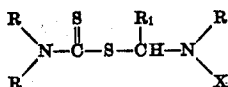
Ewald Urbchat and Franz Heckmanns, Leverkusen I. G.-Werk, Germany, assignors to Winthrop Chemical Company, Inc., New York, N. Y., a corporation of New York

No Drawing. Application April 6, 1940, Serial No. 328,376. In Germany March 16, 1939

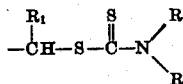
9 Claims. (Cl. 167-22)

This invention relates to new products obtainable from carbon disulfide, amines and aldehydes.

It has been found that by reacting, for instance, the intermediate products obtainable by reaction of 1 mol of a primary amine and one or two mols of an aldehyde with dithiocarbamic acids products are formed which correspond most probably to the formula



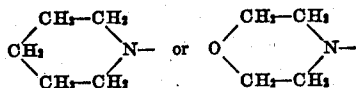
R denotes an organic residue which is linked with one carbon atom to the nitrogen atom, R₁ stands for a hydrogen atom or an organic residue and X stands either for R or the radical



R may, for instance, denote an alkyl radical including cycloalkyl and aralkyl radicals, or an aryl or a heterocyclic radical. R may, for instance, stand for methyl, ethyl, n-propyl, isopropyl, n-butyl, n-dodecyl, cyclohexyl or benzyl radicals. The said radicals may also be substituted, such as in the case of hydroxyalkyl or alkoxyalkyl radicals. R may stand for the same or different radicals. If two radicals R are bound to one nitrogen atom they may form a heterocyclic ring system. In the above formula the group



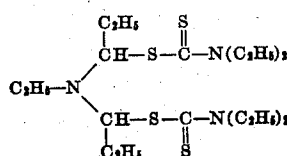
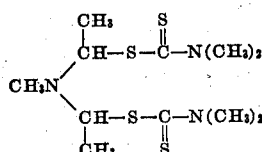
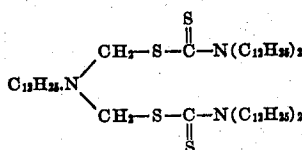
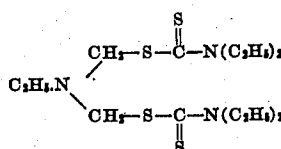
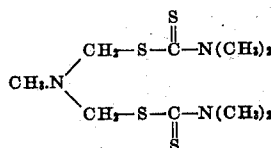
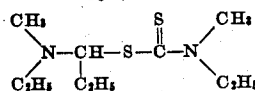
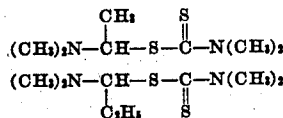
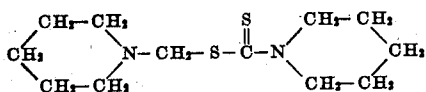
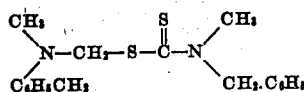
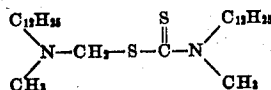
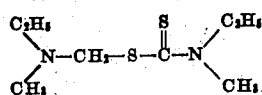
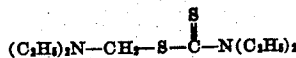
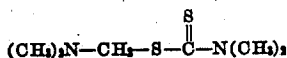
may be, for instance, a piperidyl or morpholyl residue

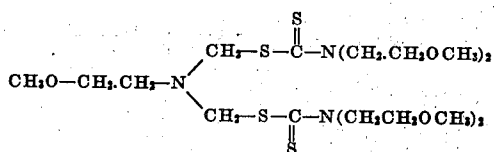


R₁ may besides a hydrogen atom denote an alkyl, cycloalkyl, aralkyl, aryl or heterocyclic group. R₁ may, for instance, be a methyl, ethyl, n-propyl or n-butyl radical.

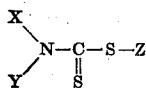
Such compounds of the above formula in which R stands for a lower alkyl radical containing from 1 to 4 carbon atoms, more particularly the methyl radical, and R₁ stands for a lower alkyl radical or a hydrogen atom have proved to be of particular value.

Compounds corresponding to the above general formula are, for instance, the following ones:

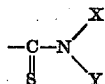




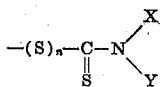
The compounds of the afore given general formula are valuable as ingredients of effective and reliable paraciticides. As contrasted to the known dithiocarbamic acid esters of the formula



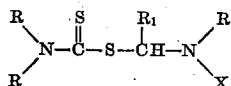
wherein X and Y stand for hydrogen, alkyl or aralkyl and Z stands for alkyl, aryl or the grouping



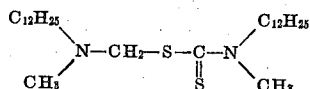
or



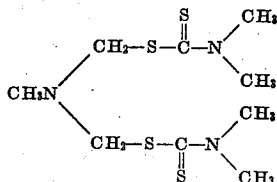
respectively, n being the integer 1, 2 or 3, they are distinguished by a much wider field of application. The lauryl-diethyl-dithiocarbamate, the most favored compound of the group of the known dithiocarbamic acid esters of the foregoing formula has hardly any action upon aphides. The known compounds are also practically unfit for seed dressing. For instance a dry seed dressing containing 2 per cent of tetramethylthiuram sulfide, when used in the usual proportion, has hardly any effect. The tetraalkylthiuram sulfides are effective only for combating fungus pests in orchards. My new compounds of the formula



are, however, effective fungicides. They are, for instance, suitable for combating, for instance, fuseladium, wood-fungi, mold fungi. Further certain representatives of this group, for instance the compound of the probable formula



may be used for exterminating insects, particularly aphides. Other compounds, such as the compound of the probable formula

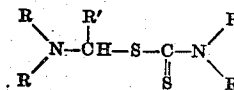


may be employed in seed dressings which are effective, for instance against fusarium.

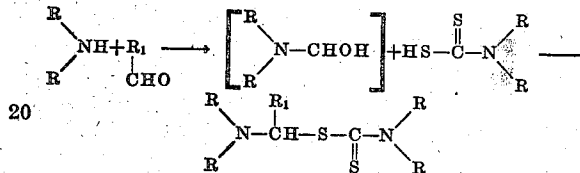
For use as parasitides the said compounds are mixed with solid or liquid inert diluents, such as talc, chalk, diatomaceous earth, gypsum, slate flour, mineral oils or aqueous emulsions of mineral oils, or organic solvents, such as chlorinated aliphatic or aromatic hydrocarbons, for example

chloroform, carbontetrachloride or monochlorobenzene.

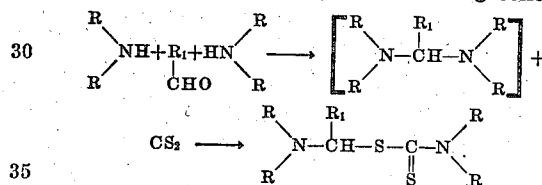
The said compounds may be prepared by several methods. The products of the general formula



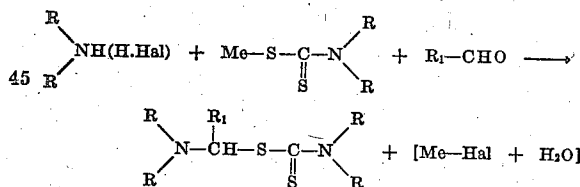
may, for instance, be obtained by reaction of 1 mol of the intermediate product—obtained by reacting 1 mol of an amine with 1 mol of an aldehyde—upon 1 mol of a dithiocarbamic acid. The reaction proceeds probably according to the following scheme:



In this reaction the dithiocarbamic acid may be replaced by the starting compounds for its formation, i. e. by a mixture containing an amine and carbon disulfide in equimolecular amounts. The reaction follows probably the following scheme:

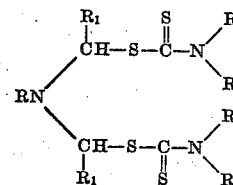


Another method of preparing these products consists in the addition of an amine-hydrohalide to a metal salt of dithiocarbamic acid, preferably a watersoluble metal salt, in the presence of an aldehyde. The reaction may be illustrated by the following probable reaction scheme:

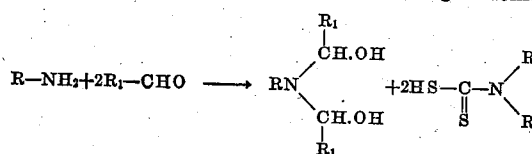


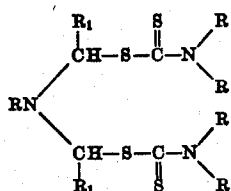
It is to be seen from this scheme that the amounts of the components are to be chosen so that 1 mol of the amine reacts with 1 mol of the dithiocarbamic acid and 1 mol of the aldehyde.

Products corresponding to the probable formula



may be prepared by reacting 1 mol of the intermediate product—obtainable by reacting 1 mol of a primary amine and two mols of an aldehyde—with 2 mols of a dithiocarbamic acid. The reaction follows probably the following scheme:





In this case, too, the dithiocarbamic acid may be replaced by the components necessary for its formation, i. e. by a mixture of an amine and carbon disulfide in equimolecular amounts.

Amines suitable for carrying out the processes described are, for instance, dimethylamine, diethylamine, di-n-propylamine, methylethylamine, methylcyclohexylamine, methyl-dodecylamine, piperidine, morpholine, monomethylamine, monoethylamine, monocyclohexylamine or benzylamine.

Suitable aldehydes are, for instance, formaldehyde, acetaldehyde, propionaldehyde or butyraldehyde.

As dithiocarbamic acids there may be cited by way of example: monomethyl-dithiocarbamic acid, dimethyl-dithiocarbamic acid, methylcyclohexyl-dithiocarbamic acid, monobenzyl-dithiocarbamic acid, piperidyl-dithiocarbamic acid or morpholyl-dithiocarbamic acid.

The following examples illustrate the invention without, however, restricting it thereto:

Example 1

A mixture is prepared containing 20% of the compound obtained by reacting 1 mol of methylamine, 2 mols of formaldehyde and 2 mols of dimethyldithiocarbamic acid (the compound melting at 75.5° C. and 80% of filling and wetting agents. This preparation is successfully used in orcharding as spray against fuscladium in a dilution of 1 per cent.

In a 0.5% dilution the said preparation is effective in viniculture against peronospora.

Example 2

A dry seed grain disinfectant is prepared by admixing 20 parts by weight of the compound referred to in Example 1 with 80 parts by weight of talc. In order to effectively combat fusarium of rye this preparation is applied in a quantity of 2-3 parts:1000 parts of seed grain.

Example 3

The compound obtainable by reaction of 1 mol of dimethylamine, 1 mol of formaldehyde and 1 mol of dimethyldithiocarbamic acid or of 2 mols of dimethylamine, 1 mol of formaldehyde and 2 mols of CS₂ (the compound melting at 42° C.) is dissolved in water to 1 per cent. Tissues which have been treated with this solution are fast to moldy stains.

The above compound stops the growth of conio-phora in a concentration of 0.06% and of fuscladium in a concentration of 0.004%.

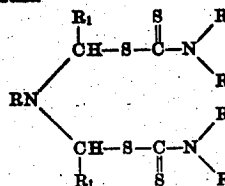
Example 4

Plants attacked by aphides are sprayed with an emulsion containing 0.2% of the compound obtained as a yellow oil by reaction of 2 mols of methyl-dodecylamine, 1 mol of formaldehyde and 1 mol of carbon disulfide. All aphides are killed.

We claim:

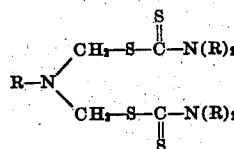
1. Insecticidal and fungicidal preparation

comprising a mixture of a compound of the probable formula



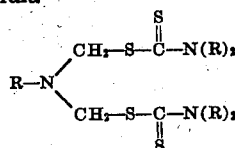
in which R stands for an alkyl radical and R₁ for a radical selected from the group consisting of the hydrogen atom and an aliphatic residue, a product which is obtainable by reacting 1 mol of an aliphatic primary amine with two mols of an aliphatic aldehyde and two mols of an aliphatic dithiocarbamic acid, and an inert diluent.

2. Insecticidal and fungicidal preparation comprising a mixture of a compound of the probable formula



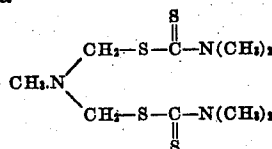
wherein R stands for an aliphatic radical, a product which is obtainable by reacting 1 mol of a primary aliphatic amine with 2 mols of formaldehyde and 2 mols of a dialkyl-dithiocarbamic acid, and an inert diluent.

3. Insecticidal and fungicidal preparation comprising a mixture of a compound of the probable formula



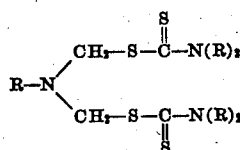
wherein R stands for an alkyl radical comprising from 1 to 4 carbon atoms, a product which is obtainable by reacting 1 mol of a primary alkyl amine comprising from 1 to 4 carbon atoms with 2 mols of formaldehyde and 2 mols of a dialkyl-dithiocarbamic acid comprising from 1 to 4 carbon atoms in the alkyl group, and an inert diluent.

4. Insecticidal and fungicidal preparation comprising a mixture of a compound of the probable formula



melting at 75.5° C., a product which is obtainable by reacting 1 mol of dimethylamine with 2 mols of formaldehyde and 2 mols of dimethyldithiocarbamic acid, and an inert diluent.

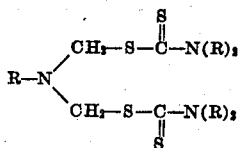
5. A compound of the formula



wherein R stands for an aliphatic radical, a product which is obtainable by reacting 1 mol of a primary aliphatic amine with 2 mols of form-

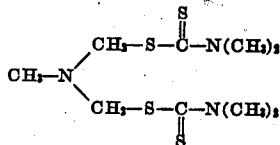
aldehyde and 2 mols of a dialkyl-dithiocarbamic acid.

6. A compound of the probable formula



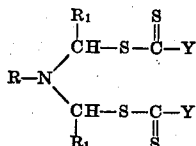
wherein R stands for an alkyl radical comprising from 1 to 4 carbon atoms, a product which is obtainable by reacting 1 mol of a primary alkyl amine comprising from 1 to 4 carbon atoms with 2 mols of formaldehyde and 2 mols of a dialkyl-dithiocarbamic acid comprising from 1 to 4 carbon atoms in the alkyl group.

7. The compound of the probable formula



melting at 75.5° C., a product which is obtainable by reacting 1 mol of dimethylamine with 2 mols of formaldehyde and 2 mols of dimethyl-dithiocarbamic acid.

8. Insecticidal and fungicidal preparation comprising a mixture of a compound of the probable formula

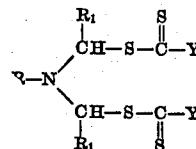


wherein Y is selected from the class consisting of



5 R is an aliphatic radical linked by one carbon atom to the nitrogen atom, R₂ represents the atoms necessary to complete a heterocyclic nitrogenous ring system, R₁ is a radical selected from the group consisting of the hydrogen atom and an aliphatic radical, a product which is obtainable by reacting 1 mol of a primary aliphatic amine with 2 mols of an aliphatic aldehyde and 2 mols of an aliphatic dithiocarbamic acid, and an inert diluent.

15 9. A compound of the probable formula



wherein Y is selected from the class consisting of



and



35 R is an aliphatic radical linked by one carbon atom to the nitrogen atom, R₂ represents the atoms necessary to complete a heterocyclic nitrogenous ring system, R₁ is a radical selected from the group consisting of the hydrogen atom and an aliphatic radical, a product which is obtainable by reacting 1 mol of a primary aliphatic amine with 2 mols of an aliphatic aldehyde and 2 mols of an aliphatic dithiocarbamic acid.

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