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CYANOVINYL DITHIOCARBAMATES

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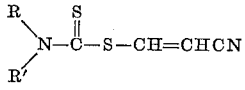
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4 Claims. (Cl. 260—455)

This invention relates to the provision of a new class of compounds. More particularly, it relates to a class of 2-cyanovinyl dithiocarbamates which can be prepared by the novel reaction of a metal salt of a dithiocarbamic acid with β-haloacrylonitrile.

It is an object of this invention to provide, as a new class of compounds, 2-cyanovinyl dithiocarbamates by a new reaction in which a metal salt of a dithiocarbamate is cyanovinylated with a β-haloacrylonitrile. It is a further object of this invention to provide a class of compounds which are useful as promoters in the benefication of ores by froth flotation. It is still a further object of this invention to provide a class of compounds which have pesticidal properties.

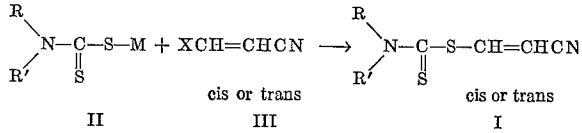
Other objects will be apparent from the following detailed description in conjunction with examples showing specific embodiments of the present invention.

The 2-cyanovinyl dithiocarbamates of the present invention may be represented by the following general Formula I:



wherein R and R′ are individually either alkyl, aryl or aralkyl groups. Alkyl groups may contain up to eighteen carbons and may be substituted with one or more (e.g., up to about three) electronegative groups such as halogen (e.g., chloro, bromo and fluoro), nitro, cyano, lower alkoxy or amino groups. Aryl groups may be monocyclic or bicyclic, i.e., phenyl, naphthyl and biphenyl having up to about five halo (e.g., chloro, fluoro and bromo), lower alkyl, cyano, amino, nitro or lower alkoxy radicals. Aralkyl groups may be monocyclic (lower alkyl) or bicyclic (lower alkyl) groups having up to about three halo (e.g., fluoro, chloro or bromo), lower alkyl, cyano, lower alkoxy, amino or nitro radicals.

Compounds of Formula I are prepared by the reaction of a β-haloacrylonitrile with a metal salt of a dithiocarbamate acid, represented by the following Equation A:



cis or trans cis or trans

II III I

wherein M is an alkali metal (e.g., potassium or sodium), R and R′ are as defined above and X is chloro or bromo. The reaction may be advantageously conducted by contacting the reactants at about ambient temperatures or lower (e.g., about 0°–40° C.). Proportions are not critical and equimolar amounts of both, or an excess of either reactant, may be used. The reaction can be carried out in aqueous medium, in which case the product separates out of solution, and the alkali metal halide stays in solution. Or else an inert polar organic solvent such as acetone or dimethylformamide may be used in which case the product remains in solution, and the salt separates as a precipitate. If desired, the product may be purified by conventional recrystallization methods employing chloroform or the like as the recrystallizing solvent.

Among the alkali metal dithiocarbamates which can be reacted with β-haloacrylonitrile are the sodium and potassium salts of the following substituted dithiocarbamic acids:

(1) N,N-dialkyldithiocarbamic acids wherein the alkyl groups are: methyl, ethyl, isopropyl, amyl, octyl, dodecyl, 2-chloroethyl, nitromethyl, methoxyethyl, and/or cyanoethyl.

(2) N,N-diaryldithiocarbamic acids wherein the aryl groups are: phenyl, α-naphthyl, β-naphthyl, 3,4,5-trimethoxyphenyl, pentachlorophenyl, p-fluorophenyl, p-nitrophenyl and/or p-cyanophenyl.

(3) N,N-diaralkyldithiocarbamic acids wherein the aralkyl groups are: benzyl, α-naphthylmethyl, 3,4-dichlorobenzyl, p-chlorophenethyl, xylylmethyl, p-cyanobenzyl, anisylmethyl and/or p-nitrobenzyl.

(4) N,N-disubstituted dithiocarbamic acids wherein the substituents are chosen from two different categories of (1), (2) and (3).

Compounds of Formula I have useful fungicidal and bactericidal properties, especially against *Bacillus mycocdes, Chaetomium globosum* and *Fusarium moniliforme.*

Additionally, such compounds have valuable metal flotation promoting properties, and can be used in conventional froth-flotation operations for the recovery of copper and zinc from sulfide ores containing these metals.

The following examples are presented to further illustrate the present invention.

EXAMPLE 1

β-Cyanovinyl diethyldithiocarbamate

To 22.5 g. of sodium diethyldithiocarbamate trihydrate in 175 ml. of acetone, there is added over a period of one hour, 8.8 g. of cis-β-chloroacrylonitrile dissolved in 25 ml. of acetone. Throughout the addition, and for one hour thereafter, the mixture is kept below 10° C., but it is then allowed to come to ambient temperature. The mixture is filtered to remove sodium chloride, and the solvent is removed in vacuo leaving 20.1 g. of a dark brown oil. The oil is dissolved in chloroform, treated, while hot, with activated carbon, filtered, and subjected to a vacuum of less than 1 mm. for about one hour while it is being heated to 80° C. The product remaining after the chloroform is evaporated off, is a brown oil, weighing 17.8 g.

EXAMPLE 2

β-Cyanovinyl diethyldithiocarbamate

The procedure of Example 1 is repeated except that trans-β-chloroacrylonitrile is used. The product is a white solid which, after recrystallization from an ether-petroleum ether mixture, melts at 53–54° C.

EXAMPLE 3

β-Cyanovinyl di-n-butyldithiocarbamate

To a solution of 22.7 g. of sodium di-n-butyldithiocarbamate in 50 ml. of water there is added over a period of 1 hour, 9.7 g. of cis-β-chloroacrylonitrile while the temperature is kept below 20° C. The mixture is then allowed to come to ambient temperature. An oil separates and is removed by extraction with chloroform. The product is isolated from the chloroform solution by evaporation of the solvent as in Example 1 to give the product as a dark-brown oil.

EXAMPLE 4

β-Cyanovinyl-N-benzyl-N-methyldithiocarbamate

By following the procedure of Example 3 except for the substitution of an equimolar quantity of sodium N-benzyl-N-methyldithiocarbamate for the dithiocarbamate used therein, the product β-cyanovinyl-N-benzyl-N-methyldithiocarbamate can be obtained.

EXAMPLE 5

Flotation of a copper ore

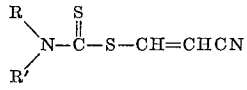
In order to show the utility of the dithiocarbamates of the present invention as flotation promoters, the compounds of Examples 1, 2 and 3 were employed in the recovery of copper from an ore from the western United States, using the following procedure. The ore sample was ground for 5 minutes at 60% solids with 0.03 lb./ton of promoter (pH 7.8). It was then conditioned for one minute with 0.09 lb./ton of cresylic acid and 0.025 lb./ton of fuel oil. The pulp was floated for 8 minutes and the tailing analyzed for residual copper, with the following results.

TABLE I

No.	Compound	Percent Cu in Tailing
1	Example 1	0.19
2	Example 2	0.34
3	Example 3	0.19

I claim:

1. A compound of the following formula:



wherein R and R′ are individually selected from the group consisting of alkyl of up to eighteen carbons containing up to about three substituents selected from the group consisting of chloro, bromo, fluoro, nitro, cyano, lower alkoxy and amino; phenyl, naphthyl and diphenyl having up to about five substituents selected from the group consisting of chloro, bromo, fluoro, lower alkyl, cyano, amino, nitro and lower alkoxy; and benzyl and naphthylmethyl having up to about three substituents selected from the group consisting of chloro, fluoro, bromo, lower alkyl, cyano, lower alkoxy, amino and nitro.

2. β-Cyanovinyl diethyldithiocarbamate.

3. β-Cyanovinyl di-n-butyldithiocarbamate.

4. β-Cyanovinyl-N-benzyl-N-methyldithiocarbamate.

References Cited by the Examiner

UNITED STATES PATENTS

2,231,265	2/41	Gaudin	209—167
2,512,669	6/50	Morrow	209—167
2,854,467	9/58	Harman et al.	260—455
2,901,498	8/59	Tilles et al.	260—455
2,914,547	11/59	Gaertner	260—455 XR

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