

UNITED STATES PATENT OFFICE

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o,o'-DI-(CARBALKOXYAMINO)-
DIPHENYLDISULFIDES

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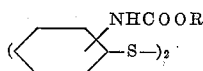
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1 Claim. (Cl. 260-470)

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This invention relates to a new group of chemical compounds. More particularly, it is concerned with a novel group of di(carboxyamino)-diphenyldisulfides.

These novel compounds may be represented generically by the type formula



wherein R is a suitable aliphatic, aralkyl, cycloaliphatic or aryl radical. Where R represents an aliphatic radical it may be either an alkyl or an unsaturated grouping. These include the methyl, ethyl, allyl, propyl, isopropyl, amyl, butyl, capryl, lauryl and the like radicals wherein there are 1-12 carbon atoms. Suitable cycloaliphatic radicals include cyclohexyl, methyl- and ethyl-cyclohexyl. Theoretically, almost any aryl radical may be present. However, the invention contemplates principally those of 6-12 carbon atoms such as the phenyl, tolyl, xylyl, diphenyl and naphthyl radicals.

While the compounds of the present invention may be prepared by any desired method, the more simple preparations are preferred. One suitable method is by the reaction of a known diaminodiphenyldisulfide with a known chloroformate of the R-OH type alcohols. By way of example, a list of typical esters will include methyl, ethyl, allyl, propyl, butyl, amyl, hexyl, phenyl, benzyl, tolyl, xylyl, biphenyl and naphthyl chloroformate.

The reaction may be carried out quite simply by adding the ester to a solution of the diaminodisulfide in a suitable solvent such as pyridine. When addition is complete and the mixture is at about room temperature, it is drowned in water. The product separates out, generally but not necessarily as an oil which soon solidifies or crystallizes. This product is then collected and purified, either by distillation or crystallization. In a few cases, notably where R is a cycloaliphatic radical, crystallization processing yields a clear resinous solid rather than definite crystals. The products are insoluble in water and hydrocarbon solvents such as heptane, petroleum ether and the like; moderately soluble in lower alcohols and ketones and quite soluble in benzene and the like.

While other uses are contemplated, the compounds of the present invention have special interest as peptizers in reducing the required milling time to obtain a desired plasticity or degree of softness to facilitate the compounding of other

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materials with any natural and synthetic rubbers which can be plasticized by mechanical working in the presence of oxygen. This property appears to be common to the entire group. A number of the compounds are particularly effective. At the same time these compounds when so used have been found to be free from objectionable odors and tendency to produce physiological reactions on the skin of the user, objections applicable to many of the less effective compounds now used for the purpose.

While there appears to be no predictable basis for the activity of these compounds, the desired peptizing properties appear to be most notable in the type wherein the (-NHCOOR) substituent is in the ortho position. The more active compounds also appear to be those wherein R is an alkyl radical of about one to six, particularly one to three, carbon atoms. Of these, for economic reasons based principally on the availability of the alcohol and high activity, the o,o'-di(carbomethoxyamino), the o,o'-di(carbethoxyamino), and o,o'-di(carballyloxyamino) diphenyldisulfides are perhaps preferable.

Preparation of the compounds of the present invention is shown in the following examples. These are intended as illustrative only and not by way of limitation. All parts are by weight unless otherwise noted.

Example 1

To a solution of 22 parts of o,o'-diaminodiphenyldisulfide in 50 parts of pyridine is added dropwise 25 parts of ethyl chloroformate. The completed admixture is allowed to stand about ½ hour and is then poured into water. An oil separates and soon crystallizes. The crystals are collected and recrystallized from ethyl alcohol. The product, o,o'-di(carbethoxyamino)-diphenyldisulfide, melts at 88°-92° C. (uncorrected).

Example 2

Substituting allyl chloroformate for the ethyl of Example 1 produces o,o'-di(carballyloxyamino)-diphenyldisulfide. Recrystallized from 2-ethylhexanol it melts at 65°-67° C. (uncorrected).

Example 3

Substituting n-propyl chloroformate for the ethyl ester of Example 1 and recrystallizing the product from n-propanol gives o,o'-di(carbopropoxyamino)-diphenyldisulfide melting at 63°-67° C. (uncorrected).

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Example 4

12.4 parts (0.05 mole) o,o'-diamino-diphenyl-disulfide was dissolved in 100 parts of methyl isobutyl ketone. This solution was placed in a flask equipped with agitator and thermometer. 53 parts of a 10% solution of sodium carbonate was then added with a small amount of Aerosol O. S. The two solutions were then agitated briskly while adding 10.3 parts (0.11 mole) of methyl chloroformate dropwise during one half hour at room temperature. Agitation was continued until the sodium carbonate layer tested neutral to alkacid paper.

The reaction mixture was then permitted to separate and the aqueous layer discarded. The methyl isobutyl ketone solution of the crude product was washed three times with 25 ml. portions of water, concentrated to half its volume and chilled in an ice bath. The precipitate, 2,2'-dithio-bis-(methyl carbanilate), when separated, washed with a little methyl isobutyl ketone and dried, melts at 108-112° C. (uncorrected).

Example 5

Replacing the ethyl chloroformate of Example 1 with phenylchloroformate yields a gummy product which does not readily crystallize. Decanting the water, taking the gum up in 2-ethylhexanol, crystallizing therefrom and recrystallizing from methanol gives an o,o'-di(carboxyphenoxyamino)-diphenyldisulfide melting at 112-114° C. (uncorrected).

Example 6

A slight excess over 2 mol parts of p-tolyl-chloroformate is added dropwise to a solution of 1 mol part of o,o'-diaminodiphenyldisulfide in pyridine, the solution being cooled in an ice bath and the rate of addition, with stirring, maintained such that the reaction temperature is less than 10° C. When admixture is complete and reaction is substantially ceased, the mixture

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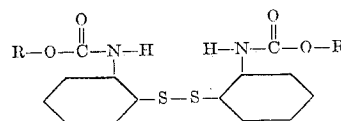
is poured into 3 N HCl. The separated reaction product is taken up in and crystallized from warm 2-ethylhexanol; extracted twice with boiling methanol and recrystallized from benzene. The product 2,2'-dithio(p-tolyl)-carbanilate, as yellow granules, melts at 135-138° C. (uncorrected).

Example 7

Substituting cyclohexylchloroformate for ethyl chloroformate in the procedure of Example 1 yields o,o'-di(cyclohexyloxyamino)diphenyldisulfide. Attempted crystallization from n-propanol, from ethylhexanol and from methylisobutyl ketone yields a clear, orange resin. No evidence of definite crystallization appears even on long standing.

We claim:

An o,o'-di(carboxyamino)-diphenyldisulfide capable of representation by the following generic formula



wherein R represents a hydrocarbon group containing from 1 to 12 carbon atoms.

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