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3,243,463

ALKYL SULFOXIDE DETERGENT

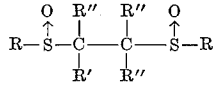
William von E. Doering, New Haven, Conn., assignor to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

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5 Claims. (Cl. 260—607)

This invention relates to novel 1,3-bis-sulfoxides and detergent compositions containing them.

In constant improvement of organic detergent compounds certain features have been found to be highly desirable. These features include resistance toward the ingredients imparting hardness to water and a high degree of detergency. Although there are a number of organic detergent compounds which have these characteristics, detergent compounds having additional desirable characteristics find a wider scope of application.

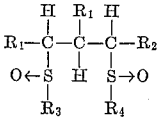
U.S. Patent 2,658,038, Wayne A. Proell, describes a class of 1,2-bis-sulfoxide detergent compounds which are relatively mild to the skin and which have effective detergency characteristics. These 1,2-bis-sulfoxides have the formula:



where R is a lower alkyl R′ is an alkyl containing 6 to 20 carbon atoms and R″ is H or lower alkyl. Attempts to formulate these 1,2-bis-sulfoxide compounds into detergent compositions containing alkaline builder materials (for the purpose of enhancing the detergency of the 1,2-bis-sulfoxide detergent compounds) showed that the 1,2-bis-sulfoxides are subject to decomposition in the presence of such alkaline materials. Apparently, the presence of an alkaline material catalyzes the decomposition of a 1,2-bis-sulfoxide into odoriferous products (e.g., methyl disulfide), thereby reducing the effective amount of detergent and creating a severe odor problem. Moreover, the 1,2-bis-sulfoxides have poor thermal stability and odoriferous decomposition products are formed at elevated temperatures, such as those encountered during transit and storage of detergent compositions, particularly in the presence of moisture, and during heat drying operations. These decomposition problems indicated that bis-sulfoxides would generally be unsuitable for alkaline built detergent compositions, particularly heat-dried compositions.

It is an object of this invention to provide novel bis-sulfoxide detergent compounds having high degrees of detergency, thermal stability and stability in an alkaline environment. It is a further object of this invention to provide built detergent compositions containing such bis-sulfoxide compounds.

It was found that these and other objects are achieved in a novel class of 1,3-bis-sulfoxides having the structure set forth below and in alkaline detergent compositions containing such compounds, which have a surprising alkaline and thermal stability, as hereinafter more fully described.



wherein one R_1 is an alkyl group containing from about 8 to about 16 carbon atoms, preferably in a straight chain, and the other R_1 is hydrogen; R_2 is a methyl or ethyl group or hydrogen; R_3 and R_4 are methyl or ethyl groups. Preferably R_3 and R_4 are methyl. The class of compounds described will hereinafter be referred to more

simply as 1,3-bis-sulfoxides. For convenience the bis-sulfoxides in which the long chain alkyl group is located midway between the alkylsulfinyl substituents are designated as symmetrical 1,3-bis-sulfoxides; where the long chain alkyl group is located on a carbon bearing an alkylsulfinyl group, the bis-sulfoxides are designated unsymmetrical 1,3-bis-sulfoxides. The preferred symmetrical 1,3-bis-sulfoxides are 2-alkyl-1,3-bis(methylsulfinyl) propanes; the preferred unsymmetrical 1,3-bis-sulfoxides are 1-alkyl-1,3-bis(methylsulfinyl) propanes; in both cases the alkyl ranges from about 8 to about 16 carbon atoms. Examples of the compounds of this invention are:

2-decyl-1,3-bis(methylsulfinyl) propane
2-tetradecyl-1,3-bis(methylsulfinyl) propane
2-hexadecyl-1,3-bis(methylsulfinyl) propane
1,3-bis(methylsulfinyl) pentadecane (or 1-dodecyl-1,3-bis (methylsulfinyl) propane)
2-dodecyl-1,3-bis(ethylsulfinyl) propane
2-dodecyl-1,3-bis(methylsulfinyl) butane (or 1-methyl-2-dodecyl-1,3-bis(methylsulfinyl) propane)
2-tetradecyl-1-(methylsulfinyl)-3-(ethylsulfinyl) pentane (or 1-ethyl-2-tetradecyl-1-(ethylsulfinyl)-3-(methylsulfinyl) propane)

2-dodecyl-1,3-bis(methylsulfinyl) propane is a preferred compound of this invention because of its optimum detergency characteristics, in both warm and cool water.

In general, the 1,3-bis-sulfoxides of this invention can be prepared by synthetic methods involving the following steps:

(1) The preparation of 2-alkyl-1,3-propanediol by reduction of the corresponding lower alkyl malonate ester, e.g., diethyl-2-alkyl malonate.

(2) Conversion of the 2-alkyl-1,3-propanediol by phosphorus tribromide or hydrobromic acid to the 2-alkyl-1,3-dibromopropane.

(3) Replacement of the 1,3-dibromo groups by methylmercapto groups by reaction of the 2-alkyl-1,3-dibromopropane with alkali metal (e.g., sodium) methyl mercaptide.

(4) Oxidation of the 2-alkyl-1,3-bis(methylmercapto) propane.

(Alkyl in the above steps ranges from C_8 to C_{16}.)

By the use of appropriate 1,3-diols having an unsymmetrical structure the corresponding unsymmetrical 1,3-bis-sulfoxides can be prepared. For example, 1,3-alkanediols can be obtained by reduction of long-chain β-keto esters. These can serve as starting material for the synthesis of unsymmetrical 1,3-bis-sulfoxides by steps similar to those outlined for the symmetrical compounds.

Alternate routes for preparation of the 1,3-bis-sulfoxides exist and will occur to those skilled in the art after reading the present description.

In 1,3-bis-sulfoxides of this invention, R_1 can be derived from naturally occurring fats and oils or from synthetic sources. Mixtures of 1,3-bis-sulfoxides are quite suitable wherein the R_1 groups vary in chain length in the C_8 to C_{16} range, as for example, the alkyl groups from coconut fatty alcohol or distilled coconut fatty alcohol.

The 1,3-bis-sulfoxides of this invention are useful per se as detergent and surface active compounds. The uses to which surface active compounds can be put are numerous and well known, e.g., preparing oil-in-water emulsions, textile treating, dyeing, flotation, preparation of rubber latex, and the like. Desirably the 1,3-bis-sulfoxides are used with alkaline builder materials to form built detergent compositions, as for example, liquid, bar, flake, granular or tabletted granular compositions. Such compositions have enhanced detergency characteristics due to the coaction in aqueous washing solution between the

1,3-bis-sulfoxides and the alkaline builder material. It is in such an alkaline medium that the surprising and advantageous usefulness of the 1,3-bis-sulfoxides, i.e., superior stability in the presence of alkaline materials, is best demonstrated. Preferably the alkaline builder in such detergent compositions is a material selected from the class consisting of water soluble inorganic alkaline builder salts, water soluble organic alkaline sequestering builder salts and mixtures thereof. Desirably the ratio of 1,3-bis-sulfoxide to the alkaline builder material is in the range of about 4:1 to about 1:20. (Parts, ratios and percentages herein are by weight.) Preferably the alkaline builder material should provide a pH of about 8 to about 11 when the detergent composition is dissolved in water.

Water-soluble inorganic alkaline builder salts used alone or in admixture are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates. (Ammonium or substituted ammonium builder salts, e.g., tri-ethanolamine, can also be used.) Specific examples of such salts are sodium tripolyphosphate, sodium carbonate, potassium carbonate, sodium tetraborate, sodium pyrophosphate, potassium pyrophosphate, sodium bicarbonate, potassium tripolyphosphate, sodium haxametaphosphate, sodium sesquicarbonate, sodium mono- and di-ortho phosphate and potassium bicarbonate. Such inorganic builder salts enhance the detergency of the subject 1,3-bis-sulfoxides.

Examples of organic alkaline sequestrant builder salts used alone or in admixture to enhance detergency are alkali metal, ammonium or substituted ammonium, aminopolycarboxylates, e.g., sodium and potassium ethylenediaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-ethylenediaminetriacetates, sodium and potassium nitrilotriacetates and sodium, potassium and triethanolammonium N-(2-hydroxyethyl)-nitrilodiacetates. Mixed salts of these polycarboxylates are also suitable. The alkali metal salts of phytic acid, e.g., sodium phytate are also suitable as organic alkaline sequestrant builder salts (see U.S. Patent 2,739,942). Also suitable are the water soluble salts of ethane-1-hydroxy-1,1-diphosphonate, e.g., the trisodium and tripotassium salts.

The detergent compositions of this invention can contain any of the usual adjuvants, diluents and additives, for example, anionic, nonionic, ampholytic, cationic or zwitterionic detergents, perfumes, anti-tarnishing agents, anti-redeposition agents, bacteriostatic agents, dyes, fluorescers, suds builders, suds depressors, and the like without detracting from the advantageous properties of the compositions. Examples of anionic detergents are sodium coconut soap, sodium dodecylbenzene sulfonate and potassium tallow alkyl sulfate. Examples of nonionic detergents are dodecyldimethylamine oxide and the condensation product of coconut fatty alcohol with 5.5 moles of ethylene oxide. An example of a zwitterionic detergent is 3 - (N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate. An example of an ampholytic detergent is sodium-3-dodecylaminopropionate. An example of an alkaline-compatible cationic detergent is dodecylmethylbenzyl sulfoxonium methosulfate.

Following are examples which illustrate the 1,3-bis-sulfoxide compounds and compositions of this invention. There are of course, modifications of these illustrations which can be made by those skilled in the art without departing from the scope of this invention as defined in the appended claims.

EXAMPLE I

A. *Preparation of diethyl 2-dodecylmalonate*

To 50.6 g. of sodium (2.2 moles) dissolved in 1600 ml. of absolute ethyl alcohol was added 352 g. (2.2 moles) of diethyl malonate, with stirring at room temperature. To the resulting solution was added, dropwise with stirring, 548 g. (2.2 moles) of dodecyl bromide. After addition was complete, the mixture was refluxed and stirred for 5 hours and allowed to stand overnight. The mixture was made neutral by the addition of glacial acetic acid. The inorganic salts were filtered off and the alcohol solvent was removed by distillation. After washing the residue three times with water and drying the organic layer over sodium sulfate, the residue was distilled through a helices-packed column. The fraction boiling at 137–142° C. at 4.7 mm. of mercury was collected. The diethyl 2-dodecylmalonate thus obtained weighed 484 g. and had refractive index $n_D^{21}=1.4400$ (yield 67%).

B. *Reduction of diethyl 2-dodecylmalonate to 2-dodecyl-1,3-propanediol*

To a slurry of 35 g. of lithium aluminum hydride in 1500 cc. of dry tetrahydrofurane was added 251 g. of diethyl 2-dodecylmalonate (0.76 mole). Addition was dropwise with stirring and at a rate to give refluxing of the solvent. After addition was complete the mixture was refluxed and stirred for 1 hour. Ethyl acetate was added to the reaction mixture to decompose the excess lithium aluminum hydride. Then aqueous 10% sulfuric acid was added cautiously and the mixture stirred until layers could be separated. The tetrahydrofurane layer was separated and cooled in a Dry-Ice bath yielding 149 g. of crude 2-dodecyl-1,3-propanediol. A single recrystallization from hexane gave 130 g. (71% yield) of the desired 2-dodecyl-1,3-propanediol melting at 70–71° C.

C. *Preparation of 2-dodecyl-1,3-dibromopropane*

2-dodecyl-1,3-propanediol (122 g., 0.50 mole) was placed in a 3-necked flask equipped with stirrer, thermometer condenser, and dropping funnel. Phosphorus tribromide (136 g., 0.50 mole) was added through the dropping funnel over a period of about 25 min. with stirring. The diol, a solid, gradually went into solution as the bromide was added, and the reaction became exothermic. The temperature rose early in the reaction to 170° C. then was reduced to 135° C. by cooling and held there for 24 hours. The temperature was then raised to 180° C. for 4 hours. Finely cracked ice and water were added to the reaction mixture and the mixture transferred to a separatory funnel and extracted with ether. The ether layers were combined with the organic layer and the combined solutions extracted with sodium carbonate solution followed by water washing. The ethereal solutions were dried over sodium sulfate, the ether evaporated, and the residue distilled through a short distilling column. Yield of the desired 2-alkyl-1,3-dibromopropane was 152.5 g. (82.5%). The product boiled at 144–146° C. at 0.4 mm. mercury and had refractive index $n_D^{25}=1.4857$.

D. *Preparation of 2-dodecyl-1,3-bis-(methylmercapto) propane*

Sodium hydroxide (56 g.) was dissolved in 80 ml. of water and 800 ml. of ethanol was added. The mixture was cooled to room temperature and held there by cooling during the addition of 63 g. (1.25 moles) of methyl mercaptan. After addition of the methyl mercaptan to the basic solution was complete, 152 g. (0.41 mole) of 2-dodecyl-1,3-dibromopropane was added dropwise at room temperature. The mixture was raised to reflux temperature and refluxed with stirring for 4 hours. The mixture was then poured into 4 liters of water and the organic phase separated. The aqueous phase was extracted with ether and the ether extract combined with the organic phase. The combined ethereal solutions were washed with water, dried over calcium chloride, and the ether evaporated. The resulting 112 g. of crude product was distilled through a short Vigreux column yielding 108 g. of the desired 2-dodecyl-1,3-bis(methylmercapto) propane boiling at 156° C. at 0.45 mm. of mercury. Refractive index $n_D^{25}=1.4868$. Density $d_4^{25}=0.9087$.

E. *Preparation of 2-dodecyl-1,3-bis(methylsulfinyl) propane*

2-dodecyl-1,3-bis(methylmercapto) propane (108 g., 0.355 mole) was dissolved in 1000 ml. of ethanol. To the resulting solution was added, dropwise with stirring (and cooling to maintain the temperature below 35° C.), 95 g. (0.82 mole) of 30% aqueous hydrogen peroxide. After the materials were mixed they were stirred for 1 hour until homogeneous and allowed to stand overnight. Palladium-charcoal catalyst was added to the reaction mixture, and the aqueous alcohol solvent was removed in vacuo . The combined solids were dissolved in hot acetone and filtered to remove the palladium catalyst. The filtrate was made up to about 1 liter with hot acetone, 500 ml. of hexane was added and the hot mixture cooled slowly to room temperature and filtered. The filter cake, 2-dodecyl-1,3-bis(methylsulfinyl) propane weighed 78.5 g. (66%) and melted at 116.5–117.5° C. Analyses of this product gave sulfur=18.81%; carbon=60.82%; and hydrogen=10.55%. (Theory for the product: sulfur=19.05%; carbon=60.71%; and hydrogen=10.71%.)

Built laundry detergent compositions containing 50% sodium tripolyphosphate, 30% sodium sulfate and 20% 2-dodecyl-1,3-bis(methylsulfinyl) propane, resulted in lipid soil detergency properties (using naturally soiled cloth and wash water at 140° F.) superior to like formulations containing sodium dodecyl benzene sulfonate and approaching like formulations containing sodium tallow alkyl sulfate. The 1,3-bis-sulfoxide was superior to both the dodecylbenzenesulfonate and the tallow alkyl sulfate in wash water at 80° F. As regards detergency, 1,3-bis-sulfoxides are at least as effective in built compositions as 1,2-bis-sulfoxide in built compositions (freshly prepared) containing, respectively, the same long chain alkyl groups.

As determined by guinea pig mildness tests, the 1,3-bis-sulfoxides of this invention, e.g., 2-dodecyl-1,3-bis-(methylsulfinyl) propane are very mild to the skin. Such guinea pig tests are described in Canadian Patent 639,398 issued April 3, 1962, to Howard F. Drew et al.

1,3-bis-sulfoxides, e.g., 2-dodecyl-1,3-bis(methylsulfinyl) propane, can be used per se as detergents for hand washing or washing of woolens in aqueous solutions of 1% concentration for example.

The symmetrical 1,3-bis-sulfoxides differ markedly in solubility characteristics from corresponding 1,2-bis-sulfoxides. Unlike the 1,2-bis-sulfoxides, the symmetrical 1,3-bis-sulfoxides exhibit extremely steep Krafft ranges. This permits the use of water as a recrystallization solvent. The unsymmetrical 1,3-bis-sulfoxides, e.g. 1,3-bis(methylsulfinyl) pentadecane, are more soluble than the corresponding symmetrical compounds.

As to bacteriostatic activity, 2-dodecyl-1,3-bis(methylsulfinyl) propane effectively controlled *M. aureus* at 4.7 p.p.m. and *E. coli* at about 150 p.p.m., being superior in this respect to 1,2-bis-sulfoxides.

To test the alkaline stability of the 1,3-bis-sulfoxides of this invention, particularly as compared to 1,2-bis-sulfoxides, 8% aqueous solutions of potassium pyrophosphate were used. A series of samples containing 3 grams of 2-dodecyl-1,3-bis(methylsulfinyl) propane in 150 ml. of the pyrophosphate solution was compared with a like series of 3 grams of 1,2-bis(methylsulfinyl) tetradecane in 150 ml. of the pyrophosphate solution. (The difference of one methylene group in the samples was found to be not significant for purposes of the comparison.) The solutions were kept at 60° C. and pH 10. A slow stream of nitrogen was used to sweep volatile products into traps containing 3% aqueous mercuric chloride. Periodically the precipitated complex of methyl disulfide with mercuric chloride which formed in the traps was removed, dried and weighed to assess the rates of formation of decomposition products. In 14 days the 1,3-bis-sulfoxide produced no precipitate. The 1,2-bis-sulfoxide produced 0.6 gram of precipitate in 1 day, 1.0 gram in 5 days and 1.1 grams in 12 days. At this point, decomposition of the 1,2-bis-sulfoxide was substantially complete. This demonstrated the surprising alkaline stability of the 1,3-bis-sulfoxide as compared to the 1,2-bis-sulfoxide.

Samples of 2-dodecyl-1,3-bis(methylsulfinyl) propane remained odor-free on storage at room temperature for three months. The odor of decomposition products is quite noticeable in sealed samples of 1,2-bis-(methylsulfinyl) tetradecane in a few days. A sample of this 1,3-bis-sulfoxide was heated in vacuo for seven hours at 150° C. with very little decomposition. A sample of this 1,2-bis-sulfoxide, however, completely decomposed in four hours upon heating in vacuo at 150° C. The 1,3-bis-sulfoxides of this invention, e.g., 2-dodecyl-1,3-bis-(methylsulfinyl) propane, show similar superior thermal stability characteristics over 1,1-bis-sulfoxides, e.g., 1,1-bis(methylsulfinyl) dodecane.

The 1,3-bis-sulfoxides of this invention can be used in effective alkaline detergent compositions having the following formulations.

Granular detergent:

	Percent
2-dodecyl-1,3-bis(methylsulfinyl) propane	10
Sodium dodecylbenzene sulfonate (the dodecyl group being derived from tetrapropylene)	10
Sodium tripolyphosphate	50
Sodium sulfate	30

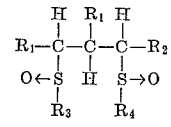
	Percent
2-dodecyl-1,3-bis(ethylsulfinyl) propane	10
Condensation product of one mole of dodecanol and twelve moles of ethylene oxide	3
Sodium pyrophosphate	57
Sodium carbonate	3
Trisodium phosphate	3
Sodium sulfate	24

Liquid detergent:

	Percent
2-decyl-1,3-bis(methylsulfinyl) butane	6
Sodium tetrapropylene benzene sulfonate	6
Potassium pyrophosphate	10
Potassium nitrilotriacetate	10
Potassium toluene sulfonate	8
Sodium silicate	3.8
Carboxymethyl hydroxyethyl cellulose	0.3
Water	Balance
2-tetradecyl-1,3-bis(methylsulfinyl) propane	5
Ethanol	10
Tetrosodium ethylenediaminetetraacetate	10
Water	75

What is claimed is:

1. 1,3-bis-sulfoxide detergent compounds having the formula



where one R_1 is an alkyl group containing from 8 to 16 carbon atoms and the other R_1 is hydrogen; R_2 is selected from the group consisting of methyl and ethyl groups and hydrogen; R_3 and R_4 are selected from the group consisting of methyl and ethyl groups.

2. The compounds of claim **1** wherein R_3 and R_4 are methyl groups.

3. 2-alkyl-1,3-bis(methylsulfinyl) propane, wherein the alkyl ranges from about 8 to about 16 carbon atoms.

4. 2-dodecyl-1,3-bis(methylsulfinyl) propane.

5. 1-alkyl-1,3-bis(methylsulfinyl) propane wherein the alkyl ranges from about 8 to about 16 carbon atoms.

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CHARLES B. PARKER, *Primary Examiner.*

A. T. MEYERS, DELBERT R. PHILLIPS, *Assistant Examiners.*