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SULFONIC ACID CONDENSATION PRODUCTS AND METHODS OF PRODUCING THE SAME

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15 Claims. (Cl. 260—293.4)

This invention relates to sulfonic acid condensation products and methods of producing the same, and more particularly to such products derived from sulfhydryl compounds and sultones.

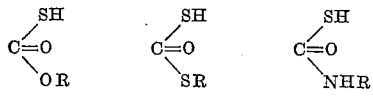
We have found that valuable new organic compounds are obtained by subjecting organic sulfhydryl compounds which contain one or more aliphatic, cycloaliphatic or aromatic hydrocarbon radicals, bonded directly or through an oxygen, sulfur or nitrogen atom to a —CO—SH or —CS—SH group, to a condensation reaction with a sultone. The sulfhydryl compounds referred to are reacted with the sultones in the form of their mercaptides or in the presence of acid-binding agents. The term "sultones" as used herein refers to cyclic sulfonic acid anhydrides of oxyalkylsulfonic acids. The products produced by the condensation reaction in accordance with this invention are substituted alkylsulfonic acid salts.

Sulfhydryl compounds which may be reacted in the form of their salts with sultones in accordance with our invention include, for example, aliphatic or aromatic thiolacids and dithioacids having the general structural formulas

or

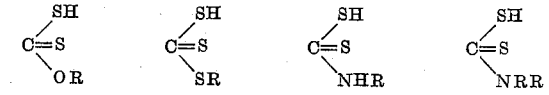
wherein R is an aliphatic or an aromatic hydrocarbon radical.

However, sultones can also be reacted with derivatives of thiocarbonic acids in accordance with our invention to yield the desired sulfonic acid compounds. The derivatives of thiocarbonic acid concerned contain a free salt-forming —CO—SH group bonded to an aliphatic or aromatic hydrocarbon radical through an oxygen, sulfur or nitrogen atom, and have the general structural formulas



wherein R represents the aliphatic or aromatic hydrocarbon radical. Examples of such derivatives of thiocarbonic acids are thiocarbonic acid ethyl ester, thiocarbonic acid-monoethylamide, and the like.

Sultones may also be reacted in accordance with our invention with the corresponding derivatives of sulfthiocarbonic acid, i. e. those compounds which contain a free salt-forming —CS—SH group bonded through an oxygen, sulfur or nitrogen atom to an aliphatic or aromatic hydrocarbon radical. Such derivatives of sulfthiocarbonic acid have the general structural formulas



wherein R represents an aliphatic or aromatic hydrocarbon radical.

Members of this group of compounds are primarily the ester salts of sulfthiocarbonic acid, known as xanthogenates, which can be readily prepared from organic oxycompounds and carbon disulfide. Examples of xanthogenates which may be employed in the reaction with sultones in accordance with our invention are methyl-, ethyl-, propyl-, allyl-, butyl-, amyl- and cetyl-xanthogenates, as well as phenyl-, cresyl-, naphthyl-, 4-chlorophenyl-, 2,4-dichlorophenyl-xanthogenates, and the like.

Other members of this group of compounds are the ester salts of trithiocarbonic acid, known as thioxanthogenates, which can be readily prepared from mercaptides and carbon disulfide. Examples of thioxanthogenates which may be employed in the reaction with sultones in accordance with our invention are the salts of ethyl-trithiocarbonic acid, isobutyl-trithiocarbonic acid, phenyl-trithiocarbonic acid, and the like.

Finally, those compounds which contain a nitrogen atom, such as the salts of dithiocarbamino acid or dithiocarbazic acid, obtained by reacting ammonia, organic amines or hydrazines with carbon disulfide, are also suitable for the reaction in accordance with our invention with sultones. Examples of such salts of dithiocarbamino acid or dithiocarbazic acid are dithiocarbamic acid, N,N-dimethyl-dithiocarbamic acid, N,N-diethyl-dithiocarbamic acid, N,N-pentamethylene-dithiocarbamic acid, N-ethyl-N-phenyl-dithiocarbamic acid, N-phenyl-dithiocarbamic acid, N-naphthyl-1-dithiocarbamic acid, N-4-chlorophenyl-dithiocarbamic acid, N-phenyl-dithiocarbazic acid, N,N-dimethyl-dithiocarbazic acid, ethylene-1,2-bis-dithiocarbamic acid, and the like.

Sultones which may be condensed with the above sulfhydryl compounds in accordance with our invention are 1,3-propane sultone or 1,4-butane sultone, or technical mixtures thereof. However, sultone derivatives comprising substituents attached to any one of the carbon atoms of the hydrocarbon chain may also be used. Such substituted sultones include, for example, 1,1-dimethyl-1,3-propane sultone (isopentane sultone). Finally, sultones in which hydrogen atoms of a cycloaliphatic or aromatic ring form a part of the sultone ring may be employed in the condensation reaction in accordance with our invention to form sulfonic acid derivatives. Substituted sultones of this type include, for example, tolyl, 1,8-naphtho-sultone, and many others.

The condensation reaction between sultones and sulfhydryl compounds in accordance with our invention, in which the sulfhydryl group is a component of a strongly acid group, takes place surprisingly rapidly and goes virtually to its theoretical completion. In most instances it is not necessary to apply any special means to start the condensation reaction, and the reaction is so vigorous that external cooling means should be provided.

While it is possible to carry out the reaction with the reactants in contact with each other in their undiluted form, the employment of suitable solvents or diluents is recommended. Substances suitable for this purpose are, for example, organic solvents such as alcohols, ketones, cyclic ethers such as dioxane, or ether-alcohols such as tetrahydrofurfural, and many others.

The sulfonic acid salts formed by the condensation reaction in accordance with our invention precipitate from the reaction mass in a very pure crystalline form

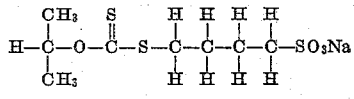
when organic solvents or diluents are present. In contrast to the very unstable thio- and dithio-compounds from which they are formed, the sulfonic acid salts produced by the reaction in accordance with this invention are surprisingly stable.

The sulfhydryl-sulfonic acid condensation products disclosed herein find their practical application in the field of accelerators for vulcanization processes and furthermore as pharmaceutical agents or intermediates for them.

The following examples will enable persons skilled in the art to understand our invention more completely. It is understood, however, that our invention is not limited to these examples or to the specific terms and conditions stated in said examples.

Example I

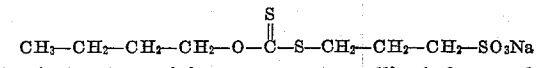
To a freshly prepared solution comprising 15.7 parts by weight sodium-isopropylxanthogenate (1/10 mol) in 300 parts by volume of propanol, 13.6 parts by weight 1,4-butane sultone (1/10 mol) were added. The solution was then warmed on a water bath. A crystalline precipitate soon formed, which when isolated was found to be the sodium salt of isopropylxanthogenic acid-n-butyl-ester-ω-sulfonic acid having the structural formula



The crystalline precipitate was then recrystallized from alcohol. After recrystallization it was found to be very stable and formed a clear solution in water. High yields were obtained.

Example II

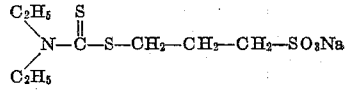
7.6 parts by weight of carbondisulfide (1/10 mol) were added to a sodium butylate solution made from 2.3 parts by weight of sodium (1/10 mol) and 250 parts by volume butanol. The mixture was agitated for ½ hour at 50° C. To this warm butyl-xanthogenate solution 12.2 parts by weight of molten 1,3-propanesultone were slowly added. A crystalline precipitate soon formed which was isolated and analyzed to be the sodium salt of n-butyl-xanthogenic acid-n-propylester-ω-sulfonic acid having the structural formula



The isolated precipitate was recrystallized from ethyl alcohol in the form of long crystalline needles. These needles were soluble in water and formed a clear solution therein. The yield was virtually quantiative.

Example III

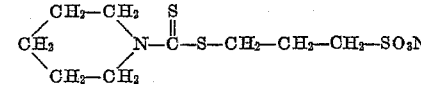
7.6 parts by weight of carbondisulfide (1/10 mol) were slowly added to a solution of 14.6 parts by weight of diethylamine (2/10 mol) in 200 parts by volume of isopropanol, while cooling the solution. Thereafter, 12.2 parts by weight of 1,3-propanesultone (1/10 mol) were added to the above solution and the mass was heated on a water bath for ½ hour. Subsequently, 100 parts by volume of an alcoholic 1 N sodium hydroxide solution were added to the warm mass. The mass was allowed to cool, whereupon a crystalline precipitate was formed. The precipitate was isolated and analyzed to be the sodium salt of N,N-diethyl-dithiocarbamic acid-n-propylester-ω-sulfonic acid having the structural formula



The isolated crystalline precipitate was purified by recrystallization from alcohol. The recrystallized product took the form of large colorless lamellae. It was stable, odorless and soluble in water, wherein it formed a clear solution.

Example IV

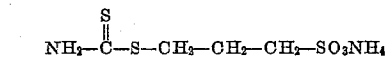
12.5 parts by weight of 1,3-propane sultone (1/10 mol) were added to a solution of 24.6 parts by weight of N,N-pentamethylene-dithiocarbamic acid (1/10 mol) in 250 parts by volume of alcohol. The mixture was warmed on a water bath for about ½ hour. Thereafter, 100 parts by volume of an alcoholic 1 N sodium hydroxide solution were added and the resulting mass was allowed to cool. A crystalline precipitate soon formed, which was filtered off and analyzed to be the sodium salt of N,N-pentamethylene-dithiocarbamic acid-n-propylester-ω-sulfonic acid having the structural formula



The crystalline reaction product was colorless, odorless, stable and formed a clear solution in water. The yield was very high.

Example V

11.0 parts by weight of ammonium salt of dithiocarbamic acid (1/10 mol), prepared in accordance with Freund and Barerach, Annalen 285, p. 201, were suspended in 200 parts by volume of isopropanol, and subsequently 12.2 parts by weight of 1,3-propane sultone (1/10 mol) were added to this suspension at 35° C. The yellow crystals of the ammonium salt of dithiocarbamic acid disappeared after a short time. A precipitate was formed which was filtered off and analyzed. It was found to be the ammonium salt of dithiocarbamic acid-propyl-ester-ω-sulfonic acid having the structural formula

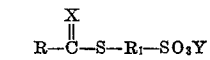


The crystalline product was recrystallized from alcohol in the form of beautifully shaped crystals.

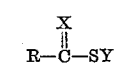
While we have given certain specific examples of our invention, we wish it to be understood that modifications and changes can be made without departing from the spirit thereof or the scope of the appended claims.

We claim:

1. The process of producing a compound having the structural formula

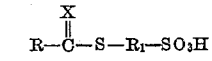


wherein R is selected from the group consisting of alkyl, aryl, alkoxy, amino, monoalkylamino, dialkylamino and piperidino, X is selected from the group consisting of oxygen and sulfur, R_1 is lower aliphatic with more than two carbon atoms and Y is selected from the group consisting of hydrogen, alkali metal and ammonium, which comprises subjecting a compound having the structural formula

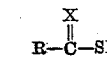


wherein R, X and Y have the meaning above indicated, to a condensation reaction with a lower aliphatic sultone, and separating the reaction product from the reaction mass.

2. The process of producing a compound having the structural formula

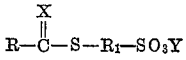


wherein R is selected from the group consisting of alkyl, aryl, alkoxy, amino, monoalkylamino, dialkylamino and piperidino, X is selected from the group consisting of oxygen and sulfur, and R_1 is lower aliphatic with more than two carbon atoms, which comprises subjecting a compound having the structural formula

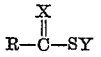


wherein R and X have the meaning above indicated, to a condensation reaction with a lower aliphatic sultone, and separating the reaction product from the reaction mass.

3. The process of producing a compound having the structural formula

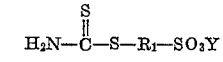


wherein R is selected from the group consisting of alkyl, aryl, alkoxy, amino, monoalkylamino, dialkylamino and piperidino, X is selected from the group consisting of oxygen and sulfur, R_1 is lower aliphatic with more than two carbon atoms and Y is hydrogen which comprises subjecting a compound having the structural formula



wherein R, X and Y have the meaning above indicated, to a condensation reaction with a lower aliphatic sultone in the presence of an acid-binding agent, and separating the reaction product from the reaction mass.

4. The process of producing a compound having the structural formula



wherein R_1 is alkyl and Y is selected from the group consisting of hydrogen and alkali metal, which comprises subjecting a compound selected from the group consisting of dithiocarbamic acid and its alkali metal salts to a condensation reaction with an alkyl sultone, and separating the reaction product from the reaction mass.

5. The process of producing isopropylxanthogenic acid-n-butylester-ω-sodium sulfonate, which comprises subjecting sodium-isopropylxanthogenate to a condensation reaction with 1,4-butanesultone, and separating the reaction product from the reaction mass.

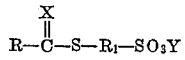
6. The process of producing butylxanthogenic acid-n-propylester-ω-sodium sulfonate, which comprises subjecting sodium-butylxanthogenate to a condensation reaction with 1,3-propanesultone, and separating the reaction product from the reaction mass.

7. The process of producing N,N-diethyldithiocarbamic acid-n-propylester-ω-sodium sulfonate, which comprises subjecting N,N-diethyl-dithiocarbamic acid to a condensation reaction with 1,3-propanesultone, neutralizing the condensation product with sodium hydroxide, and separating the neutralized product from the reaction mass.

8. The process of producing N,N-pentamethylene-dithiocarbamic acid-n-propylester-ω-sodium sulfonate, which comprises subjecting N,N-pentamethylene-dithiocarbamic acid to a condensation reaction with 1,3-propanesultone, neutralizing the condensation product with sodium hydroxide, and separating the neutralized product from the reaction mass.

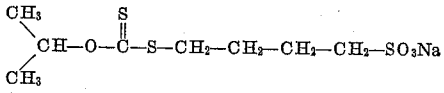
9. The process of producing dithiocarbamic acid-n-propylester-ω-ammonium sulfonate, which comprises subjecting ammonium-dithiocarbamate to a condensation reaction with 1,3-propanesultone, and separating the reaction product from the reaction mass.

10. Compounds having the structural formula

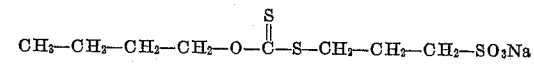


wherein R is selected from the group consisting of alkyl, aryl, alkoxy, amino, monoalkylamino, dialkylamino and piperidino, X is selected from the group consisting of oxygen and sulfur, R_1 is lower aliphatic with more than two carbon atoms and Y is selected from the group consisting of hydrogen, alkali metal and ammonium.

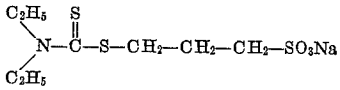
11. As a new compound,



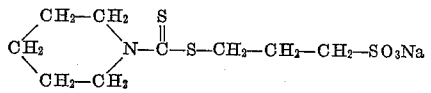
12. As a new compound,



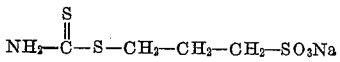
13. As a new compound,



14. As a new compound,



15. As a new compound,



No references cited.