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PRODUCTION OF SELENOMERCAPTANS

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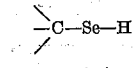
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7 Claims. (Cl. 260—429)

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This invention relates to a new and useful method of preparing selenomercaptans and salts of the same. The invention is more particularly directed to the preparation of aliphatic selenomercaptans containing eight or more carbon atoms in the aliphatic radical attached to selenium, and salts of the same.

Selenomercaptans, i. e., compounds having in the molecule the group



have utility as intermediates in the preparation of other compounds of selenium. Salts of the same are similarly useful. The aliphatic selenomercaptans containing not less than five, preferably eight to thirty carbon atoms in the aliphatic radical attached to selenium, are also valuable antioxidants for mineral lubricating oils and the like. Polyvalent metal salts of these aliphatic selenomercaptans are useful as motor oil "detergents"; i. e., as additives to promote engine cleanliness and to inhibit piston ring sticking.

Such methods as are described in the literature for preparing aliphatic selenomercaptans are by reaction of sodium or magnesium hydroselenide [NaHSe or $Mg(HSe)_2$] with an aliphatic halide or an aliphatic metal sulfate, or by reaction of aluminum selenide with an alcohol at elevated temperatures. See for example, J. Newton Friend's "Textbook of Inorganic Chemistry," vol. XI, part IV, page 1 (1937). These methods are disadvantageous because dialkyl selenides and dialkyl diselenides are formed by side reactions. This necessitates the recovery of the selenomercaptan by distillation or some other method. When applied to the preparation of high molecular weight selenomercaptans, i. e., those containing about 8 to 10 carbon atoms or more, these methods of the prior art are especially disadvantageous because of the tendency of the high molecular weight selenium compounds to decompose on distillation. Further, any method requiring the use of a metal hydroselenide requires the use of hydrogen selenide, which is disadvantageous because hydrogen selenide is difficult to generate and handle and is poisonous.

It is an object of this invention to provide an improved method of preparing selenomercaptans and salts thereof.

It is a further object of this invention to provide a method of preparing aliphatic selenomercaptans and salts of the same, which avoids the necessity of using hydrogen selenide and which

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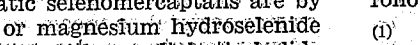
is characterized by a good yield of selenomercaptan and a minimum of side reactions and unwanted products.

It is a particular object of this invention to provide a simple, economical method of preparing high molecular weight aliphatic selenomercaptans and salts of the same, containing eight or more carbon atoms in the hydrocarbon radical, which avoids the use of hydrogen selenide, provides a good yield of selenomercaptan and yields a product which can be purified without distillation.

It is a further particular object of the invention to provide a means of producing metal salts of selenomercaptans by a simple procedure involving reduction of a readily available selenium compound and recovery of the desired metal salt from the reaction product without isolating any intermediate product.

Other objects will be apparent from the following description and the appended claims.

I have discovered that organic selenomercaptans can be prepared by reducing an organic selenocyanate in an acid medium by means of a metallic reducing agent, the reaction being as follows:

(I) 

wherein R is an organic group.

All or a large part of the cyanogen will be decomposed. Since a metallic reducing agent is used, the reaction solvent or medium will contain metallic ions. If it is desired to isolate the free selenomercaptan, it can be separated by simple physical means from the acid medium, as described in more detail hereinbelow. On the other hand, and in an important embodiment of the invention, if it is desired to produce the salt of the selenomercaptan and the reducing metal, this can be conveniently accomplished by neutralizing the excess acid of the acid medium with any suitable base capable of forming a more soluble selenomercaptide than the reducing metal.

A specific example will serve to illustrate these two embodiments of the invention. In this example, the reagents are illustrative and can be substituted as described in more detail hereinbelow.

Thus, dodecyl selenocyanate ($n\text{-}C_{12}H_{25}SeCN$) is added to an aqueous solution of sulfuric acid, the latter being used in excess of the amount theoretically required to complete the reaction. The mixture is heated to and maintained under reflux and is agitated while zinc dust is gradually

added. After completion of the reaction, the product is treated in either of two ways, depending upon whether dodecyl selenomercaptan ($n\text{-}C_{12}H_{25}SeH$) or zinc dodecyl selenomercaptide [$(n\text{-}C_{12}H_{25}Se)_2Zn$] is desired:

(*a*) If dodecyl selenomercaptan is desired, the reaction mixture is extracted with ethyl ether and the solvent evaporated on a steam bath.

(*b*) If zinc dodecyl selenomercaptide is desired, the reaction mixture (after filtration, if necessary, to remove solid impurities), is neutralized with caustic soda solution, whereupon zinc sulfate dissolved in the aqueous layer causes precipitation of zinc dodecyl selenomercaptide, probably by the series of reactions:

$$2NaOH+2C_{12}H_{25}SeH\rightarrow 2C_{12}H_{25}SeNa+2H_2O$$

$$ZnSO_4+2C_{12}H_{25}SeNa\rightarrow (C_{12}H_{25}Se)_2Zn+Na_2SO_4$$

The method of the invention is especially advantageous in the preparation of high molecular weight aliphatic selenomercaptans, those containing eight or more carbon atoms in the molecule, and their salts with polyvalent, reducing metals. A minimum of by-products are produced. If it is desired to recover the selenomercaptan, this can be done by physical means as in embodiment (*a*), above. If it is desired to recover a zinc or other polyvalent, reducing metal salt, this can be done by embodiment (*b*), above. In either case, the necessary steps of recovery are reduced to a minimum and distillation of the product is made unnecessary.

By "aliphatic" radical as used herein and in the claims is meant a radical attached to selenium by a non-benzenoid carbon atom. Thus, benzyl selenocyanate, lauryl selenocyanate and cyclohexyl selenocyanate are all aliphatic selenocyanates, and upon reduction yield aliphatic selenomercaptans, within the meaning of the term "aliphatic" as used herein and in the claims.

The reduction of the selenocyanate, as stated, is carried out by means of a metallic reducing agent in an acid medium. The preferred reducing agent is zinc, which may be in any suitable form, such as mossy zinc or zinc dust. Of the two, zinc dust is preferred. Examples of other suitable reducing agents are aluminum, magnesium and iron.

The preferred acids for rendering the reaction medium acid are sulfuric acid and hydrogen chloride. Acetic acid may be used as may other organic and inorganic acids.

The reaction medium will usually comprise a solvent, such as water, alcohol, acetone, ethyl ether or dioxane, but in the case of acetic acid, glacial acetic may be used, functioning both as the source of hydrogen and as the reaction medium.

The concentrations of acid used and the manner of conducting and controlling the reduction reaction will vary according to the acid used and considerations of convenience. Thus, where sulfuric acid is used, an aqueous solution of 10% to 70% concentration may be used, 40 to 60% being preferred. In such case, the selenocyanate is preferably mixed with the aqueous acid, held at an elevated temperature or under reflux, and agitated while the reducing agent is added gradually, at such rate as to control the reaction. However, it is possible, though less desirable, to add zinc and selenocyanate to water, hold under reflux and agitate and gradually add concentrated sulfuric acid.

Where hydrogen chloride is used, the solvent or reaction medium is preferably alcohol. The selenocyanate and zinc are preferably added to the alcohol and the mixture is refluxed and agitated while gaseous HCl is passed into it. By controlling the rate of addition of HCl gas, the reaction can be controlled. Preferably, the reaction mixture is kept saturated with HCl, but concentrations as low as 10% may be used. Variants of this embodiment of the invention will be apparent to one skilled in the art.

Where acetic acid is used, it is preferably used in the same manner as sulfuric acid, concentration of the aqueous solution preferably being 20 to 80% but, as stated, even glacial acetic acid may be used.

It will be understood that in cases where the whole body of acid is added before the start of the reaction, the acid concentration will diminish as the reaction proceeds. Also, while refluxing temperatures are preferred, lower temperatures, usually 170° to 260° F., depending upon the solvent, may be employed.

Frequently, where a metallic reducing agent, such as zinc dust, is added to a heated mixture of acid medium and selenocyanate, the reduction will not have been completed upon adding all the reducing agent. In such cases, it is expedient to add a further quantity of acid and continue heating or refluxing and agitation until the reduction reaction is completed or substantially completed.

Thereafter, the product is worked up as indicated. If the selenomercaptan produced by the reaction is liquid, it will separate out as an oily layer; or if a solid, as a crop of crystals upon cooling. This oily layer or crop of crystals can be recovered by decantation, filtration or extraction with a solvent, such as ethyl ether, petroleum thinner or benzene. It can be used as such, e. g., as an antioxidant, or it can be purified as by fractional distillation; by recrystallization from a solvent such as a mixture of benzene and acetone or benzene and ethyl alcohol; or by treating it with aqueous caustic alkali, adding to the resulting aqueous solution or dispersion an aqueous solution of a polyvalent metal salt (such as zinc acetate) to precipitate a polyvalent metal selenomercaptide and regenerating the free selenomercaptan from its polyvalent metal salt.

Alternatively, where the salt of the selenomercaptan and the reducing metal is desired, there may be added to the reaction mixture water (if the mixture is non-aqueous) and a neutralizing agent such as sodium or potassium hydroxide, sodium or potassium carbonate, sodium or potassium acetate or ammonia, in quantity sufficient to neutralize or substantially neutralize the acid. This brings about formation of a water-insoluble polyvalent reducing metal selenomercaptide (e. g., zinc selenomercaptide where zinc has been used as the reducing agent), which can be recovered by filtration, dried and used as such (e. g., as a motor oil detergent) or purified, as by recrystallization from a suitable solvent such as a mixture of benzene and ethyl alcohol.

The following specific examples will serve further to illustrate the practice and advantages of the invention:

Example 1.—Preparation of 2-ethylhexyl selenomercaptan and zinc salt thereof

2-ethylhexyl selenocyanate was prepared by reacting 1150 grams of crude 2-ethylhexyl chloride with the calculated amount of potassium

selenocyanate in refluxing alcohol. Fifteen hundred and eighty grams of the resulting crude 2-ethylhexyl selenocyanate, containing 5.3 moles of 2-ethylhexyl selenocyanate based on selenium content, were heated and stirred at 170°–180° F. with 1610 ml. of 50% (by weight) sulfuric acid. Six hundred and fifty-five grams of zinc dust were added in small portions over a period of 30 minutes. When the addition was complete, 462 ml. of concentrated sulfuric acid dissolved in 1132 ml. of water were added, the temperature was increased to 210° F. and stirring was continued for two hours. The cooled reaction mixture was extracted with petroleum ether, the extract was dried and freed of solvent on the steam bath. The residue, crude 2-ethylhexyl selenomercaptan, was purified and the zinc was prepared as follows: The crude selenomercaptan was stirred with 2130 ml. of absolute ethyl alcohol and 556 grams of zinc acetate dissolved in 2130 ml. of hot 50% ethyl alcohol were added slowly. A white precipitate of zinc 2-ethylhexyl selenomercaptide formed and was filtered off, washed with acetone and ethyl alcohol and dried. Analysis. Found: Se=31.6%, 31.9%, Zn=13.9%. Theoretical: Se=35.2%, Zn=14.5%. The product weighed 1152 grams, representing a yield of 90.5% based on selenium. A sample of this zinc 2-ethylhexyl selenomercaptide was dissolved in hot benzene and treated with concentrated hydrochloric acid under nitrogen. The benzene layer was washed with water, dried over anhydrous sodium sulfate and distilled. 2-ethylhexyl selenomercaptan distilled at 98°–100° C. under a pressure of 30 mm. of mercury. Analysis: Found, Se=40.8%; theoretical, Se=40.8%. N_D^{20}=1.4760.

Example 2.—Preparation of dodecyl seleneomercaptan and zinc salt thereof

Potassium selenocyanate was prepared by dissolving 153 grams of metallic selenium in a solution of 130 grams of potassium cyanide in 100 ml. of water. After removal of the water by heating at reduced pressure, 1000 ml. of ethyl alcohol and 481 grams of crude dodecyl chloride were added and the mixture was stirred and heated at reflux for 27 hours. The product was extracted with petroleum ether, the extract was dried over anhydrous sodium sulfate and freed of solvent on the steam bath. The product (crude dodecyl selenocyanate) weighed 601 grams and contained 23.5% Se. Five hundred and ninety grams of this product were heated and stirred at 210° F. with 670 ml. of 50% (by weight) sulfuric acid. Two hundred and twenty grams of zinc dust were added over a period of 15 minutes. A mixture of 192 ml. of concentrated sulfuric acid and 470 ml. of water was added and stirring and heating at 230° F. was continued for one hour. After cooling, the product was extracted with ethyl ether and freed of solvent on the steam bath. 502 grams of crude dodecyl selenomercaptan assaying 25.5% Se were obtained. The crude product was purified and the zinc salt was prepared as follows: A solution of 198 grams of zinc acetate in 1000 ml. of 50% ethyl alcohol was added slowly to a mixture of 490 grams of the crude dodecyl selenomercaptan and 1000 ml. of hot ethyl alcohol. The precipitated zinc dodecyl selenomercaptide was collected on a filter, washed with water and alcohol and dried in vacuo over calcium chloride. Analysis. Found: Se=23.3%; Zn=9.4%. Theoretical: Se=23.1%; Zn=11.6%. The product weighed 525 grams representing a yield of 81% based on selenium. A sample of this zinc dodecyl selenomercaptide was dissolved in hot benzene and treated with concentrated hydrochloric acid under nitrogen. The benzene layer was washed with water, dried over anhydrous sodium sulfate and distilled. The fraction boiling between 160° and 170° F. at 10 mm. of mercury was collected. Analysis: Found: Se=30.3%. Theoretical: Se=31.6%. N_D^{20}=1.4747.

Example 3.—Preparation of paraffin selenomercaptan

Paraffin selenocyanate was prepared by reacting 563 grams of chlorinated match wax (a low melting point paraffin wax, chlorinated to 10.6% Cl) with the reaction product of 59.3 grams of selenium and 48.7 grams of potassium cyanide. The reaction was carried out in refluxing ethyl Cellosolve for 22 hours and the reaction mixture was diluted with water and extracted with ethyl ether. The ether extract was dried over sodium sulfate, filtered and freed of solvent. The weight of the product was 628 grams assaying 9.9% Se, representing a quantitative yield of paraffin selenocyanate. Reduction to the selenomercaptan was carried out by passing a stream of anhydrous hydrogen chloride into a refluxing mixture of 292 grams of the paraffin selenocyanate, 52 grams of zinc dust and 420 ml. of 95% ethyl alcohol over a period of one hour and forty minutes. The reaction mixture was diluted with water, extracted with petroleum ether and the extract was dried with sodium sulfate, filtered and freed of solvent. Yield of product was 265 grams containing 8.0% selenium. The product (paraffin selenomercaptan) was waxy and similar in appearance to the original match wax.

Selenomercaptans are prone to oxidation by atmospheric oxygen. It is, therefore, advisable to blanket reaction mixtures and solutions containing them in nitrogen (or other inert gas) until such time as the final product is obtained and can be placed in a closed container. This was, in fact, done in the preparations described above.

The method of the invention is applicable to the reduction of other selenocyanates to selenomercaptans; e. g., the reduction of methyl, ethyl, n- and iso-propyl, n- and sec.-butyl, n- and sec.-amyl, n- and sec.-octyl, cetyl sec.-heptadecyl, cyclohexyl, methyl-cyclohexyl, benzyl, phenyl and cetyl phenyl selenocyanates to the corresponding selenomercaptans.

The method of the invention is especially advantageously applied to the preparation of complex mixtures of aliphatic selenomercaptans (and salts of the same) such as prepared by chlorinating a mixture of petroleum hydrocarbons (naphtha, kerosene, lubricating oil fractions, paraffin wax), condensing the chlorinated product with sodium selenocyanate to produce a mixture of aliphatic selenocyanates and reducing the mixture to a mixture of aliphatic selenomercaptans. Such mixtures of petroleum hydrocarbons are predominately mixtures of paraffinic and/or naphthenic hydrocarbons; they have average molecular weights ranging from 110, more or less, in the case of naphtha to 360, more or less, in the case of paraffin wax. Some of these hydrocarbon mixtures, such as paraffin wax, are semi-solid or solid at atmospheric temperature; e. g., at 77° F.

Such mixtures may be chlorinated to any desired percentage of chlorine content, preferably

about one gram atom of chlorine per average gram molecular weight of the mixture, and the chlorinated mixture may be reacted with potassium selenocyanate to produce any desired degree of substitution of selenocyanate radical for chlorine. Ordinarily, about 40 to 70% of the chlorine will be substituted. Accordingly, the end product of the method of the invention (i. e., a mixture of high molecular weight aliphatic selenomercaptans), will contain more or less chlorine according as replacement of the chlorine by selenium is more or less complete.

Other replaceable groups, e. g., bromine and other metal selenocyanates, e. g., sodium selenocyanate, may replace chlorine and sodium selenocyanate, respectively.

The method of the invention is especially advantageous as applied to preparation of such complex mixtures of high molecular weight aliphatic selenomercaptans (and salts of the same), since the desired product is itself a complex mixture not readily adapted to purification by fractional distillation (except to isolate cuts boiling in a narrow range of temperatures), and the method of the invention provides a means of preparing such a mixture free or relatively free from unwanted by-products, such as aliphatic selenides and diselenides.

Thus, paraffin wax ranging in average molecular weight from about 300 to 400 can be converted in good yield by the method of the invention to a valuable mixture of selenomercaptans relatively free from other compounds of selenium.

In this and other similar embodiments of the invention, wherein the starting material is a complex mixture of hydrocarbon, which is then chlorinated, the amount of chlorine (or other replaceable group) in the final product can be controlled in the second step of the reaction, i. e., the reaction of the chlorinated material with potassium (or other metal) selenocyanate. By using higher reaction temperatures or longer reaction periods, or both, a low chlorine product is obtained. Correspondingly, by using lower reaction temperatures and/or shorter reaction periods, a high chlorine product is obtained.

I claim:

1. A two-step process for the production of a substantially water insoluble selenomercaptan salt of a metal which comprises reacting said metal with an acid in the presence of an organic selenocyanate selected from the group consisting of the alkyl, cycloalkyl, alkaryl and arylselenocyanates and thereafter neutralizing the acidic reaction mixture with a base selected from the group consisting of the alkali metal hydroxides, the basic salts of the alkali metals, and ammonia.

2. The two-step process of claim 1 in which the selenocyanate is an alkyl selenocyanate.

3. The two-step process of claim 1 in which the metal is zinc.

4. The two-step process of claim 1 in which the acid is sulphuric acid.

5. A process for the production of selenomercaptans which comprises forming a mixture of an organic selenocyanate and an aqueous solution containing from 40% to 60% by weight of sulphuric acid and introducing into said mixture a metal reactive with said sulphuric acid, while the mixture is maintained at an elevated temperature, said organic selenocyanate being selected from the group consisting of the alkyl, cycloalkyl, alkaryl and arylselenocyanates.

6. The process of claim 5 wherein the metal employed is zinc.

7. The process of claim 5 wherein the organic selenocyanate is an alkyl selenocyanate.

WILLIAM T. STEWART.

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