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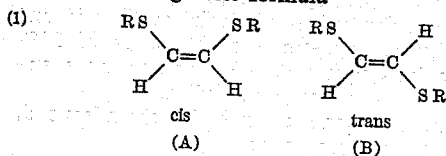
PROCESS FOR PREPARATION OF DIALKYL-MERCAPTOETHYLENES

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This invention relates to a novel process for the preparation of cis, trans mixtures of 1,2-dialkylmercaptoethylenes of the generic formula



where R is an alkyl group of from 1-6 carbons.

The process described herein is a convenient and economical method for the manufacture of trans enriched mixtures of 1,2-dialkylmercaptoethylenes. These compounds are easily oxidized over to the corresponding 1,2-dialkylsulfonylethylene compounds which have value as fungicides and are seed treating agents. The term "alkyl" as used in this case has reference to less than 7 carbon atoms.

The process of this invention possesses a number of advantages over the prior art.

For one thing, all steps involved here employ low cost, commercially available raw materials. Previous methods of preparing 1,2-dialkylmercaptoethylenes involve the interaction of the less available cis-dichloroethylene with sodium alkylmercaptide in an alcohol to give almost entirely the cis-1,2-dialkylmercaptoethylene. The trans-dichloroethylene does not react with sodium alkylmercaptide. Thus trans-1,2-dialkylmercaptoethylene is a difficultly producible chemical.

In order to obtain, for example, the trans 1,2-dipropylsulfonylethylene, reported to be a more effective fungicide and seed treatment agent than the corresponding cis isomer, isomerizing oxidative methods and prolonged autoclaving in the pressure of iodine or cis 1,2-dipropylmercaptoethylene during and after oxidation are required. This invention describes a process which gives a cis-trans mixture containing at least 40% of the trans isomer.

Under optimum cracking conditions of the 1,1,2-trialkylmercaptoethane one may get a desired mixture of cis, trans 1,2-dialkylmercaptoethylenes containing up to 70 weight percent or more of trans isomer. In general, however, the processes of this invention produce a mixture containing at least 40 weight percent of trans isomer.

These isomers can be separated by careful fractional distillation or by oxidation to the sulfones in acetic acid. The trans 1,2-dialkylsulfonylethylene is almost insoluble in 50% cold acetic acid, whereas the cis isomer is relatively soluble.

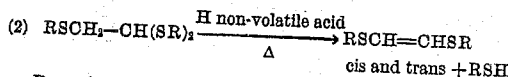
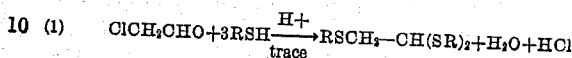
Another advantage of the present invention is that these processes enable one to prepare the trialkylmercaptoethanes without solvent using only a trace of a protonic acid, alkylthiols and chloroacetaldehyde. A description of the invention will now be given in detail below.

The products of this invention are prepared by heating in the presence of a non-volatile acid certain trialkylmercaptoethane intermediates. These are formed by re-

2

acting chloroacetaldehyde with an excess of an alkylmercaptan. An important chemical property of the cis, trans 1,2-dialkylmercaptoethylenes of this invention is their ready conversion by oxidation to the corresponding 1,2-dialkylsulfonylethylenes.

The preparation of cis, trans-1,2-dialkylmercaptoethylenes by the process of this invention is a two-step sequence of reactions, as follows:



Reaction 1.—1,1,2-trialkylmercaptoethanes form slowly initially with the evolution of heat, water and hydrochloric acid when an excess of an alkyl mercaptan containing from one to six carbon atoms is gradually added to rapidly stirred chloroacetaldehyde to control reaction temperature. Obviously, in order to obtain maximum theoretical conversion at least a 3:1 mole ratio of alkyl mercaptan to chloroacetaldehyde is used, however, a slight excess beyond such ratio, say 10% of the mercaptan, is convenient to use to force the reaction to a completion. With the higher boiling alkylmercaptans it may be more convenient to reverse the order of addition of reagents. In any event, the order of addition is not important for the rate of reaction or course of reaction; only to the convenience and economy of the reaction.

Although hydrochloric acid is formed during this Reaction 1, the reagents react smoother and immediately if a protonic acid (i.e. any acid having an ionizable proton), as for example concentrated hydrochloric, hydrobromic, hydrofluoric, phosphoric, or sulfuric acid, is added to the chloroacetaldehyde prior to treatment with the alkylmercaptan. A catalytic amount of protonic acid is all that is required in the range of $\frac{1}{10}$ to $\frac{1}{1000}$ mole ratio of the protonic acid to the moles of acetaldehyde used (i.e. 0.1 to 0.001 to 1). A preferred protonic acid is hydrochloric.

The reaction characteristically occurs over a wide temperature range between 10° and 100° C., but it is generally more efficient to operate slightly above room temperature at a range of, say, about 35-60° C. with moderate external cooling applied as and if needed to the reaction vessels to avoid loss by evaporation. With the more volatile alkyl mercaptans, it is preferred to operate in the range of 35-45° C.

It is convenient to lead in the mercaptan (as for example methylmercaptan) slowly beneath the surface of a stirred chloroacetaldehyde. By controlling the rate of addition of the mercaptan, one can also curb the heat-up of the reaction. Stirring or other form of agitation is desirable during the reaction to avoid localized heat-up of the reagents. In general, uniform temperatures during this reaction are desirable. When all the alkylmercaptan is added, the reaction mixture is best stirred further until there is no longer any evidence of exothermic heat of reaction.

While no special purity is needed for chloroacetaldehyde, generally it is more economical to use an aqueous grade of chloroacetaldehyde available commercially, such as a 40-45% aqueous solution. The water solvent in this case need not be removed before use. Alkyl mercaptans react with aqueous solutions of chloroacetaldehyde containing protonic acid of the kind and amount described above to give high yields of the 1,1,2-trialkylmercaptoethanes, etc. For the aqueous system mole ratios of the reactants and optimum temperature ranges are as described for the no-solvent system above. Generally, the aqueous reactions are more convenient to run.

3

At this point the trialkylmercaptoethane reaction product contains water, hydrochloric acid, and whatever acid was added to initiate the reaction. The stirred mixtures are neutralized by the addition of sufficient preferably concentrated aqueous base (as for example NaOH, KOH, Na_2CO_3 , $\text{Ca}(\text{OH})_2$ and the like).

In general, an aqueous base having a concentration in excess of 0.1% is preferred. Neutralization is continued until the pH of the mixture rises to from $7\frac{1}{2}$ to 8. Preferably, base addition is made so that the reaction temperature remains below 60°C .

External cooling is required to allow for a convenient rate of neutralization without excessive heating of the reaction. The reaction is preferably cooled to room temperature (say below 5 to 20°C .), allowed to settle and the trialkylmercaptoethane siphoned away from the slightly basic aqueous layer.

Of course, it is not necessary to cool to separate out this oily product.

To dry the oily product, conventional drying agents such as anhydrous magnesium sulfate, calcium chloride, molecular sieve and the like can be slurried, for example, in the oily product and removed by filtration. A technical grade 1,1,2-trialkylmercaptoethane is thus obtained in essentially quantitative yields and is of satisfactory quality for use in the next step of this process.

Reaction 2.—1,1,2-trialkylmercaptoethanes distill normally under reduced pressure without decomposition. It has been found, however, that 1,1,2-trialkylmercaptoethanes decompose smoothly when heated in the presence of certain acids to cis and trans mixtures of the corresponding 1,2-dialkylmercaptoethylene and alkylthiol.

To accomplish this decomposition, it is preferred to use a non-volatile acid catalyst since the alkylmercaptan and 1,2-dialkylethylene which evolve during the heating step can then be collected directly without volatile acid contamination.

Preferably, the non-volatile acid is also non-soluble in the cracking residue; this enables one to separate out this acid catalyst by decantation following cracking.

Examples of non-volatile non-soluble acid catalysts which can be used effectively to decompose the trialkylmercaptoethanes to the desired ethylenes include sodium bisulfate, sodium dihydrogenphosphate, toluene sulfonic acid, acidic resin ion exchangers, sulfuric acid, and phosphoric acid.

Generally, from 1.0 to 10% by weight of the non-volatile acid in relation to the weight of trialkylmercaptoethane is added. It is preferred to pulverize the solid acids to allow for maximum contact. Generally, an ordinary distillation vessel (glass or stainless steel) is suitable for the operation of this decomposition step providing the trialkylmercaptoethane and the non-volatile acid mixture can be stirred if desired while being distilled. Although the expected decomposition will occur at atmospheric conditions, prolonged heating causes undesirable tar formation (presumably polymerization of the dialkylmercaptoethylene). These tars can be avoided to a great extent by heating a stirred trialkylmercaptoethane and non-volatile acid mixture under reduced pressure in the range of 10–25 mm. Hg pressure. Sparging the reactor slowly with nitrogen helps further to lessen tar formation.

The temperature at which the alkyl mercaptan begins to "crack out" from a given trialkylmercaptoethane varies for the individual compounds of this invention. The lower boiling starting materials begin to "crack out" the alkylmercaptan at lower temperatures than the higher boiling trialkylmercaptoethanes. Generally, however, the alkyl mercaptans will start to evolve (at 15–25 mm. Hg) when pot temperatures reach 95° – 160°C . A practical constant rate of alkylmercaptan removal can be achieved by gradually increasing the decomposition temperature during the course of the reaction in the range of 10 – 30°C . beyond the initial "cracking temperature."

4

When all the expected alkylmercaptan has been distilled away, isolated and recycled for use in Reaction 1 above, the still-pot contains a technical grade (85–95% active) of a cis, trans mixture of 1,2-dialkylmercaptoethane containing the desired trans enrichment.

A hot tube reactor can be used very effectively. By passing a trialkylmercaptoethane through a 5 inch bed of small granular sodium bisulfate particles (i.e. smaller than 10–20 mesh, U.S.D.A. sieve) heated in the range of 150° – 250°C . for 0.5 to 2.0 seconds contact time under a reduced pressure of 10–25 mm. Hg unusually high conversion to the desired trans enriched mixture of 1,2-dialkylmercaptoethylene is achieved per pass with a minimum of undesirable tar formation.

The cracking residue need not be removed from the acid catalyst but this residue is of sufficient purity to be used directly for the conversion to the cis, trans 1,2-dialkylsulfonylethylenes.

Conversion of the pot residue to such sulfonyl ethylenes can be accomplished by diluting the pot residue with from 2 to 5 parts by weight of glacial acetic acid and adding at reflux temperature a slight excess of 30% hydrogen peroxide (aqueous). The desired trans sulfonyl ethylene crystallizes out on standing.

In order that the invention can be better understood, the following examples are given:

Example 1

A 12 liter flask equipped with stirrer, thermometer, condenser and dropping funnel is charged with 3627 g. of chloroacetaldehyde (practical grade Eastman Kodak product 40–45% aqueous solution) and 15 g. of concentrated HCl at room temperature. Propanethiol 3900 g., is added to the above stirring mixture rapidly initially, via a dropping funnel, until the reaction pot temperature reaches 50°C . This is generally achieved by adding 1000 ml. of propanethiol in about 20 minutes. External cooling is applied to the reaction pot so that the remaining quantity of propanethiol is added at 50 – 52°C . pot temperature in about 1.5 hours. Vigorous stirring is continued without external cooling until the reaction temperature decreases to room temperature. At this point, a solution of 816 g. of sodium hydroxide dissolved in 1700 g. of water is added to the reaction slowly with stirring and cooling at a rate sufficient to keep the pot temperature below 55°C . The reaction is cooled to room temperature, allowed to settle and the product (upper oil layer) siphoned away from the lower aqueous (slightly basic) layer. The oil product is slurried with sufficient magnesium sulfate (anhydrous) to dry and clear the oil and finally filtered through a coarse glass-sintered funnel. A total of 4087 g. of technical grade tripropylmercaptoethane is obtained.

A flask equipped with stirrer, thermometer, and a condenser topped with a simple distilling head is charged with 20 parts of sodium bisulfate crystals (partially pulverized) and 1008 parts of the crude tripropylmercaptoethane obtained in step 1 above. This mixture is sparged with nitrogen, stirred and heated under reduced pressure (water pump, 15–20 mm. Hg. absolute) to a temperature of about 100°C . in about 15 minutes. At this point, propanethiol (off gas) began to condense on a Dry-Ice acetone cold-finger condenser arranged in series with the above mentioned distilling head. The pot temperature is increased slowly to 120°C . so that the take-off rate of propanethiol is about 1 drop a second. Further heating is applied slowly to a maximum of 139°C . pot temperature in order to maintain an efficient decomposition rate. Generally, about 10% more than calculated propanethiol (some water, starting material and product carried over with $\text{C}_3\text{H}_7\text{SH}$) is collected in a 4.5 hour heating period.

The pot residue is cooled to room temperature, siphoned away from the solid sodium bisulfate, and distilled in another set-up through a 10" Vigreux column at 0.5 mm. First fraction distilling at 80 – 103°C .

(0.5 mm.) is collected to give an average yield of 82% yield of cis, trans mixture of 1,2-dipropylmercaptoethylene ($n_D^{25}=1.5300-1.5318$). The distillation pot contained a heavy black tar-like oil (discarded).

Recharge of fresh tripropyl mercaptoethane to the first apparatus with 10 g. fresh NaHSO_4 catalyst can be made without clean-up of the set-up.

Examples 2 through 9 are prepared by the procedure of Example 1 above. The amounts of the alkylmercaptan reagents used are equivalent on a molecular basis to propanethiol of Example 1 above. The alkyl mercaptans used and the products obtained are listed in tabular form below.

Examples 2 through 9

Ex. No.	Alkyl Mercaptan	Cis, trans, Product
2-----	methylmercaptan-----	1,2-dimethylmercaptoethylene.
3-----	ethylmercaptan-----	1,2-diethylmercaptoethylene.
4-----	isopropylmercaptan-----	1,2-di-isopropylmercaptoethylene.
5-----	n-butylmercaptan-----	1,2-di-n-butylmercaptoethylene.
6-----	iso-butylmercaptan-----	1,2-di-iso-butylmercaptoethylene.
7-----	n-amylmercaptan-----	1,2-di-n-amylmercaptoethylene.
8-----	iso-amylmercaptan-----	1,2-di-iso-amylmercaptoethylene.
9-----	n-hexylmercaptan-----	1,2-di-n-hexylmercaptoethylene.

I claim:

1. In a process for making mixtures of cis and trans 1,2-dialkylmercaptoethylenes containing at least 40 weight percent of trans isomer, the steps of

(1) contacting chloroacetaldehyde with an alkylmercaptan while maintaining a uniform temperature of from 35 to 60° C.,

(2) adding sufficient aqueous base to the reaction mixture to raise the pH to 7.5 and then separating the oily product from the mixture, and

(3) heating the oily product of step (2) with from 1.0 to 10 weight percent (based on such oily product) of an acid catalyst which is nonvolatile and nonsoluble in the reaction medium, said acid having an ionizable proton, while maintaining pressures of from 10-25 mm. Hg and temperatures of 95 to 160° C., so as to crack such oily product and to distill off alkylmercaptan.

2. In a process for making mixtures of cis and trans

1,2-dialkylmercaptoethylenes containing at least 40 weight percent of trans isomer, the steps of

(1) contacting chloroacetaldehyde with an alkylmercaptan while maintaining a uniform temperature of from 35 to 60° C., in the absence of solvents and in the presence of an acid having an ionizable proton, the mole ratio of such acid to chloroacetaldehyde being from 0.1 to 0.001:1,

(2) adding sufficient aqueous base to the reaction mixture to raise the pH to 7.5 and then separating the oily product from the mixture, and

(3) heating the oily product of step (2) with from 1.0 to 10 weight percent (based on such oily product) of an acid catalyst which is nonvolatile and nonsoluble in the reaction medium, said acid having an ionizable proton, while maintaining pressures of from 10-25 mm. Hg and temperatures of 95 to 160° C., so as to crack such oily product and distill off alkylmercaptan, said acid catalyst being non-soluble in the cracking residue.

3. In a process for making mixtures of cis and trans 1,2-dialkylmercaptoethylenes containing at least 40 weight percent of trans isomer, the steps of

(1) contacting chloroacetaldehyde with an alkylmercaptan while maintaining a uniform temperature of from 35 to 60° C., said chloroacetaldehyde initially being dissolved in water in an amount up to that sufficient to produce a saturated solution at reaction temperatures, said contacting being in the presence of an acid having an ionizable proton, the mole ratio of such acid to chloroacetaldehyde being from 0.1 to 0.001:1,

(2) adding sufficient aqueous base to the reaction mixture to raise the pH to 7.5 and then separating the oily product from the mixture, and

(3) heating the oily product of step (2) with from 1.0 to 10 weight percent (based on such oily product) of an acid catalyst which is nonvolatile and nonsoluble in the reaction medium, said acid having an ionizable proton, while maintaining pressures of from 10-25 mm. Hg and temperatures of 95 to 160° C., so as to crack such oily product and distill off alkylmercaptan, said acid catalyst being non-soluble in the cracking residue.

No references cited.