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## PROCESS FOR PREPARING ORGANIC SULFIDES

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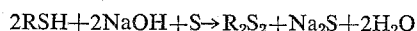
Claims priority, application France, Feb. 5, 1962,

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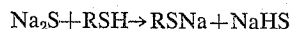
6 Claims. (Cl. 260-608)

This invention relates to the production of organic sulfides and more particularly concerns dialkyl or diaryl-disulfides.

In the manufacture of dialkyldisulfides by prior art methods, it has been customary to react a mercaptan with sulfur in aqueous sodium hydroxide, using one molecule of sodium hydroxide per molecule of mercaptan, in accordance with the following equation:



However, in practice secondary reactions take place, namely the formation of sodium mercaptide:



as well as formation of polysulfides, particularly trisulfide  $\text{R}-\text{S}-\text{S}-\text{S}-\text{R}$ .

Therefore these processes leave something to be desired from the standpoint of both yield of dialkyl-disulfide and purity of the product.

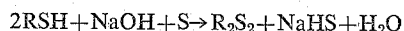
It is an object of this invention to provide a process which constitutes an improvement over the prior art in these particulars.

It is another object of this invention to provide a process for the production of disulfides free from the impurities which result from the side reactions mentioned above.

A further object of this invention is to provide the product with a good yield.

A still further object of the invention is to provide an economy from the standpoint of the necessary base, namely sodium hydroxide.

In the practice of the invention sulfur is reacted, in the presence of an alkali metal hydroxide or/and an alkaline earth metal hydroxide, with a mercaptan, in aqueous medium, the proportion of the base being equal, or nearly equal, to one half gram equivalent per molecule of mercaptan, as will be evident from the following equation:



in which the necessary base is only one half of that used in the prior art methods.

In the preferred form of the invention the organic phase which forms is separated from the aqueous phase, after the above mentioned reaction takes place.

As can be seen, the aqueous phase which is formed consists of a solution of hydrosulfide, NaHS in the case of sodium, instead of sulfide ( $\text{Na}_2\text{S}$ ) as in the prior art methods.

When a direct or indirect use is provided for the thus formed hydrosulfide, the aqueous phase formed can be used for that purpose, after having been separated from the organic phase; in such case, the production of disulfide  $\text{R}_2\text{S}_2$  is highly economical from the standpoint of the consumption of base, as only  $\frac{1}{2}$  mole of NaOH per mole of RSH is required for the reaction, in place of the equimolar quantities required for the practice of prior art methods.

On the other hand, when no use is provided for the hydrosulfide, the aqueous phase formed is neutralized with a base in order to recover the corresponding sulfide. In such case, the process of the invention is accomplished by a three step operation involving (1) the mercaptan is

2

first reacted with one gram equivalent of base for two gram moles of mercaptan; (2) the organic phase which forms is separated; (3) additional base is then added to the separated aqueous solution, in order to transform the hydrosulfide into sulfide; and (4) the sulfide is recovered.

In the preferred form of the invention, the mother-liquor from the separation of sulfide may be reemployed as an aqueous medium for a fresh reaction between the mercaptan, sulfur and the base.

A particular feature of the practice of the invention in its preferred form consists in the fact that sulfur is first dissolved in the aqueous medium intended to react with the mercaptan, in order to cause the reaction of the latter to proceed rapidly. As a result a solution of sulfur, and not a mere suspension of solid sulfur is produced, and made to react with the mercaptan. Formation of the solution is enhanced by reemploying the mother-liquor of sulfide separation, the sulfur being substantially more soluble in this liquor; on the other hand, whatever mercaptan remains dissolved in the mother-liquor, is thus recycled.

Although the concentration of the base in the reaction mixture may vary, it must however be sufficiently high, preferably between about 5 N and 10 N.

Sulfur is preferably used in theoretical amount, i.e. one atom of S for 2 moles of mercaptan.

Desirably the reaction between the mercaptan, the base and sulfur is operated under a pressure higher than 1 atmosphere. Thus the reaction may take place with liquid mercaptan if a sufficiently high pressure is maintained for a given temperature. The extent of pressure to maintain depends of course upon the nature of the particular mercaptan or mercaptans used; for example pressures from 3 to 10 atm. may be applied in the case of methylmercaptan made to react at temperatures between 5 and 30° C. The temperatures used may vary, for example, from -25° C. and +80° C.; very good results are obtained at room temperature i.e. about 20° C. The process may be operated by steps, or continuously if suitable stirring is applied to the reaction mixture, especially in the region where contact starts between the mercaptan and the aqueous base solution.

The following examples illustrate but do not limit the invention. Although these examples illustrate the use of sodium hydroxide, other bases particularly alkali metal or alkaline-earth metal hydroxides may also be used. Similarly preparation of dimethyl disulfide is given as one of the embodiments of the process of the invention while the same may also be applied to the production of other disulfides, namely ethyl, propyl, butyl, isobutyl, phenyl, cyclohexyl, etc. disulfides.

### EXAMPLE 1

100 g. of NaOH is dissolved in 550 g. of water and the solution obtained is stirred with 80 g. of flowers of sulfur. A stream of mercaptan  $\text{CH}_3\text{SH}$  is then passed through the solution, at room temperature until saturation occurs in about 10 minutes after 250 g. of the latter compound has been absorbed. The two liquid phases thus obtained are separated in a 233 g. organic phase and a 739 g. aqueous phase. By distillation of the organic phase, 209.6 g. of dimethyldisulfide  $(\text{CH}_3)_2\text{S}_2$  and 11 g. of heavier compounds which can be recycled, are obtained; 9.5 g. of mercaptan is also found. 100 g. of sodium hydroxide is added to the aqueous phase and after crystallization, 238 g. of sodium sulfide  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  separates out.

The crystallization mother-liquor is concentrated and another 212 g. of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  is obtained which separates out and makes a total of 450 g of recovered crystalline sodium sulfide. The transformation rate of mercaptan into dimethyldisulfide is 85.5%, the molar yield of the

latter being 95%, based on the mercaptan used, including the mercaptan recovered during distillation of the organic phase and during concentration of the aqueous mother-liquor which contained its solution.

#### EXAMPLE 2

The process is similar to the first part of Example 1 except that the aqueous mother-liquor remaining after crystallization of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  is not concentrated but filtered, and 100 g. of NaOH dissolved in 160 g.  $\text{H}_2\text{O}$  added thereto.

Another load of 80 g. of sulfur is dissolved in the aqueous liquid thus obtained and mercaptan is passed through, as in Example 1. After separation of the organic and aqueous phases, sodium hydroxide is added to the latter to promote crystallization of the sulfide  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , its mother-liquor being thereafter recycled in the next operation. Four successive preparations are thus achieved, the sodium sulfide mother-liquor being recycled. After the last preparation, the solution of hydrosulfide obtained is not neutralized with sodium hydroxide.

The material balance of these successive cyclic operations is the following:

##### Involved

Sulfur—322 g., that is 10.07 gram atoms  
NaOH—565 g., that is 14.12 moles  
 $\text{CH}_3\text{SH}$ —1139.8 g., that is 23.8 moles

##### Compounds obtained

$\text{CH}_3\text{SH}$  recovered—121.3 g., that is 2.53 moles  
 $(\text{CH}_3)_2\text{S}_2$ —913.2 g., that is 9.72 moles  
 $(\text{CH}_3)_2\text{S}_3$ —18 g., that is 0.15 moles  
Crystalline  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ —1146.3 g., that is 4.77 moles  
S containing aqueous solution—4.88 gram atoms  
NaHS—4.42 moles

The resulting yield of sodium hydroxide is 99%:

|                                                                         |                        |
|-------------------------------------------------------------------------|------------------------|
|                                                                         | Moles                  |
| NaOH recovered in $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ----- | $2 \times 4.77 = 9.54$ |
| NaOH recovered in NaHS -----                                            | 4.42                   |

|             |       |
|-------------|-------|
| Total ----- | 13.96 |
|-------------|-------|

NaOH used—14.12 moles  
(13.96/14.12)100=99

The yield of sulfur is 97.5%:

|                                                                      |            |
|----------------------------------------------------------------------|------------|
|                                                                      | Gram atoms |
| S recovered as $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ----- | 4.77       |
| S recovered as aqueous solution -----                                | 4.88       |
| S as $(\text{CH}_3)_2\text{S}_3$ -----                               | 0.15       |
|                                                                      | 9.80       |

S involved—10.07 at.  
(9.8/10.07)100=97.5

The yield of methylmercaptan is 93.8%:

|                                                                           |       |
|---------------------------------------------------------------------------|-------|
|                                                                           | Moles |
| $\text{CH}_3\text{SH}$ recovered -----                                    | 2.53  |
| $\text{CH}_3\text{SH}$ transformed into $(\text{CH}_3)_2\text{S}_2$ ----- | 19.44 |
| $\text{CH}_3\text{SH}$ transformed into $(\text{CH}_3)_2\text{S}_3$ ----- | 0.30  |
|                                                                           | 22.27 |

$\text{CH}_3\text{SH}$  involved—23.8  
(22.27/23.8)100=93.8

The latter yield may be improved if more serious precautions are taken against losses due to volatilization of methylmercaptan.

It is to be noted that, following the process of the invention, the molar proportion of dimethyl trisulfide  $(\text{CH}_3)_2\text{S}_3$  in the product obtained is very low, namely 0.15 mole in  $9.72 + 0.15 = 9.89$  moles, i.e. about 1.5%. From the above data it will be seen that the rate of transformation of methylmercaptan in dimethyldisulfide is 81.8% and the yield is 91.5% including the recycled

mercaptan. However, it seems that the 6.2% of mercaptan missing in the material balance are due to losses of this very volatile compound, which could be avoided by appropriate precautions; thus the real rate of transformation would be 87.5% and the yield would be 98.5%.

The characteristics of the dimethyldisulfide obtained in this example are the following:

|                                      |              |
|--------------------------------------|--------------|
| Boiling point under 760 mm. Hg ----- | ° C. 109–111 |
| $n_D^{20}$ -----                     | 1.5261       |
| $d_4^{20}$ -----                     | 1.059        |

#### EXAMPLE 3

Through a glass column 110 cm. high and of 3.4 cm. diameter, filled with Raschig rings to the level of 500 ml. methyl mercaptan and a sulfurizing solution (described below) are sent in a continuous stream. The reactive compounds are introduced in parallel streams at the bottom of the column, while at its top, the liquid runs through a filter and into a decanting pot, the gas, i.e. mercaptan in excess, being sent to a recovering apparatus.

At the bottom of the column, a water circulation coil maintains the temperature of the reaction mixture at 20° C.

The sulfurizing solution contains:

|                             |             |
|-----------------------------|-------------|
| $\text{Na}_2\text{S}$ ----- | moles-- 1   |
| S -----                     | at-- 3.5    |
| NaOH -----                  | moles-- 2.5 |
| $\text{H}_2\text{O}$ -----  | g-- 868     |

This solution and the methylmercaptan, which are both introduced in the liquid state, remain within the column for 20 minutes, before reaching the outlet at the top of the column.

Equilibrium having been reached after 2 hours, the following material balance was observed in the course of one hour's further operation.

the course of one hour's further operation:

|                                                |       |
|------------------------------------------------|-------|
| Introduced:                                    | Grams |
| Aqueous solution -----                         | 1120  |
| Methylmercaptan -----                          | 380   |
| Recovered:                                     |       |
| Aqueous solution -----                         | 1133  |
| Organic phase -----                            | 349.6 |
| Mercaptan recovered as a gas -----             | 17.4  |
| Mercaptan recovered in the organic phase ----- | 69.8  |
| Dimethyldisulfide produced -----               | 268.2 |
| Dimethyltrisulfide -----                       | 11.6  |

The rate of transformation of mercaptan into dimethyldisulfide is 70%. The recycling of unreacted mercaptan brings the yield up to 96.8%.

What we claim is:

1. A process for the preparation of an organic disulfide selected from the group consisting of dimethyl-, diethyl-, dipropyl-, dibutyl-, di-isobutyl-, diphenyl-, and dicyclohexyl-disulfide, which comprises reacting sulfur, a mercaptan selected from the group consisting of methyl-, ethyl-, propyl-, butyl-, isobutyl-, phenyl- and cyclohexylmercaptan and an alkali metal hydroxide in an aqueous solution, in the proportion of 0.5 gram equivalent of said alkali metal hydroxide and 0.5 gram atom of sulfur per mole of said mercaptan.

2. The process as defined in claim 1, in which the reaction is carried out at temperatures between -25° C. and 80° C. and under pressures of from 1 to 10 atmospheres.

3. The process as defined in claim 1, in which the sulfur is dissolved in said aqueous solution prior to reaction with the mercaptan and the alkali metal hydroxide.

4. A process for the production of dimethyl-disulfide, which comprises reacting sulfur, methylmercaptan and an alkali metal hydroxide in an aqueous solution, in the

5

proportions of 0.5 gram atom of the sulfur and 0.5 gram equivalent of the alkali metal hydroxide per mole of the methylmercaptan, at temperatures within the range of from 5° to 30° C. and under pressures of from 1 to 10 atmospheres.

5 5. The process as defined in claim 4, in which the sulfur is dissolved in said aqueous solution prior to reaction with the methylmercaptan and the alkali metal hydroxide.

10 6. A cyclic process for the production of dimethyl-disulfide, which comprises:

- 15 (a) reacting sulfur, methylmercaptan and sodium hydroxide in an aqueous solution, in the proportion of 0.5 gram atom of sulfur and 0.5 gram equivalent of sodium hydroxide per mole of methylmercaptan, at temperatures within the range of from 5° to 30° C. and under pressures of from 1 to 10 atmospheres;
- (b) separating the resulting organic liquid layer containing dimethyl-disulfide from said aqueous solution;

6

(c) adding sodium hydroxide to the residual aqueous solution containing sodium hydrosulfide to convert the same to sodium sulfide;

(d) crystallizing sodium sulfide from said aqueous solution and separating the residual mother liquor therefrom;

(e) dissolving sulfur in said mother liquor and recycling the resulting sulfur-containing aqueous solution to step (a) for further reaction.

#### References Cited by the Examiner

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