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METHOD OF PREPARING ORGANIC DISULPHIDES

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13 Claims. (Cl. 260—16)

This invention relates to the oxidation of mercaptans.

It involves, among other things, the discovery that organic mercaptans may be readily and effectively oxidized to disulphides by the use, among others, of water-soluble persulphates such as the ammonium and alkali-metal persulphates. In accordance with the teachings of the invention, organic disulphides are prepared by oxidizing the corresponding mercaptans, preferably dissolved or otherwise dispersed in a liquid medium, by means of an oxidizing agent or a mixture of oxidizing agents of the kind described. Ordinarily the liquid medium in which the mercaptan to be oxidized is dissolved or otherwise dispersed is water, alcohol or an aqueous solution of alcohol; but any other suitable liquid medium may be employed instead.

The preferred method of practicing the invention contemplates the treatment in an aqueous medium of the desired mercaptan with the theoretical quantity of ammonium persulphate. The persulphates are of especial value for the purposes of the invention, although, as hereinafter pointed out, other substances such as the perchlorates and permanganates may be used instead. In the practice of the invention, it is in general necessary only to admix the solution or other dispersion of the desired mercaptan with ammonium persulphate or other desired oxidizing agent. In some cases, it will be found helpful to permit the mixture to stand at room temperatures for a period of time; in others, to heat the mixture. In order to obtain the best yields, it will usually be found desirable to agitate the mixture, this being particularly desirable in cases in which a suspension of the mercaptan, rather than a solution, is employed.

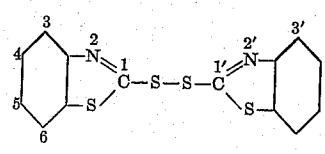
If a persulphate be employed as the oxidizing agent, the acidity or basicity of the solution or other dispersion of the mercaptan makes little difference. In the case of the perchlorates and permanganates, however, it is generally desirable that the solution or other dispersion of the mercaptan be either neutral or acid in character at or shortly after the addition of the oxidizing agent. This is conveniently accomplished by adding an inorganic acid, such as sulphuric acid, to the solution or other dispersion of the mercaptan either in conjunction with the oxidizing agent or else shortly after its addition. If desired, inorganic acids may be employed even with the persulphates, but they are not necessary.

The mercaptans to which the invention relates are mercaptans in which the —SH group is intact and substituted mercaptans in which the hydrogen atom of the —SH group is replaced by an inorganic radical. In general, any partly or completely alcohol-soluble mercaptan having the formula $(RS)_nM$, wherein R is an organic radical, M is an inorganic radical and n is one or more, may be employed in the practice of the invention. Since the reaction proceeds to best advantage when the mercaptan to be oxidized is dissolved in the particular liquid medium employed, mercaptans soluble in the liquid vehicle are preferred in the practice of the invention, but partly and difficulty soluble mercaptans may be employed with good results in the form of suspensions. Typical of the inorganic radicals represented by M are hydrogen, ammonium, sodium potassium, lithium, calcium, strontium and barium. The radical R may be any cyclic or acyclic radical, aliphatic or aromatic.

The invention will be illustrated in detail in the following examples.

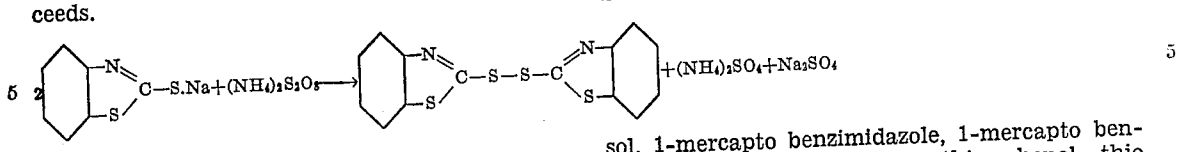
Example 1

In the preparation of 1, 1′ dibenzothiazyl disulphide, having the formula



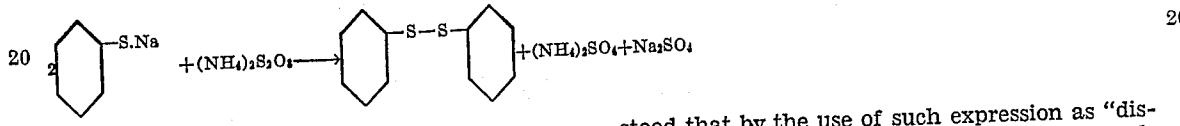
aqueous solutions of ammonium persulphate and sodium benzothiazyl mercaptide may be mixed, preferably in the proportion of two mols of the mercaptide to one mol of the persulphate. A white precipitate results at once which, on filtering and drying, melts at approximately 170–171 degrees C. The yield is practically quantitative. The equation for the reaction may be represented for present purposes as follows, it being understood that it is not known in what

stages the actual mechanics of the reaction proceeds.



Example 2

In a similar manner, diphenyl disulphide may be obtained in quantitative yield by treating a solution of thiophenol in an excess of an aqueous caustic, for example, sodium hydroxide, with an aqueous solution of ammonium persulphate. The product is a white, crystalline solid melting at 59–60 degrees C., the preparation of which may be represented by the following equation:

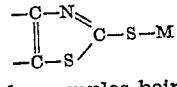


Example 3

25 grams of 1-mercaptobenzothiazole are dissolved in 200 cc. of water containing 6.3 grams of sodium hydroxide. A small amount of insoluble material is filtered off. To the solution is added, with stirring, a solution of 8.7 grams of potassium permanganate and 9.3 grams of sulphuric acid in 200 cc. of water. A precipitate forms which contains manganese dioxide and dibenzothiazyl disulphide. The manganese dioxide may be removed by the addition of 100 cc. of 5% sulphuric acid after which the dibenzothiazyl disulphide is obtained in a yield of 22.9 grams in somewhat impure form.

It will be understood that varying amounts of oxidizing agent and acid, if used, may be employed as desired. In each case the preferred amounts will generally be best determined by experimentation. Usually, however, the desirable proportions will be in the neighborhood of those illustrated herein. It will also be understood that when an agent is used to prevent equilibrium in the reaction, others instead of sulphuric acid may be employed. Examples are hydrochloric acid, nitric acid, phosphoric acid, acetic acid, etc. Advantageously the agent is added to the reaction mixture in an amount at least sufficient to neutralize all the alkali formed. Larger amounts may of course be employed and in some cases yield better results.

In addition to the mercaptans disclosed, any other mercaptan which will dissolve to a greater or less extent in alcohol may be dispersed in a liquid medium and similarly oxidized to the corresponding disulphide by treating it with a persulphate, permanganate or perchlorate and, if desired, with an acid. Among others, any thiazyl sulphide having the grouping



may be employed, examples being 1-mercapto 3-tolyl thiazole, 1-mercapto 4-tolyl thiazole, 1-mercapto 3-5-xylyl thiazole, 1-mercapto 5-methoxy benzothiazole, 1-mercapto 5-ethoxy benzothiazole, 1-mercaptothiazole, 1-mercapto 4-chlor benzothiazole, 1-mercapto 5-chlor benzothiazole, 1-mercapto 4-nitro benzothiazole, 1-mercapto 5-nitro benzothiazole, 1-mercapto 5-amino benzothiazole, 1-mercapto naphthothiazole and its various ring substituents, 1-mercapto 3-phenyl thiazole and 1-mercapto 3-phenyl benzothiazole. Still other mercaptans are thio phenol, thio cresol, 1-mercapto benzimidazole, 1-mercapto benzoxazole, thio xylol, amino thio phenol, thio naphthol, ethyl mercaptan, butyl mercaptan and propyl mercaptan.

While examples of the compounds to be oxidized and of the oxidizing dispersions have been given, it is to be understood that these examples are only illustrative and not limitative of the invention and that the invention is limited only by the accompanying claims. It is to be understood that by the use of such expression as "dispersing in a liquid medium", reference is made generically to both suspensions and true solutions. It is intended that the patent shall cover by suitable expression in the appended claims whatever features of patentable novelty reside in the invention.

This application is, in part, a continuation of application Serial No. 540,498, filed December 11, 1931.

What I claim is:

1. A method of preparing aryl thiazyl disulphides which comprises oxidizing the corresponding thiazyl mercaptide with ammonium persulphate.

2. A method of preparing di(benzothiazyl) disulphide which comprises oxidizing 1-mercaptobenzothiazole with ammonium persulphate.

3. A method of preparing a di(aryl thiazyl) disulphide which comprises oxidizing the corresponding 1-mercapto aryl thiazole with ammonium persulphate.

4. The process of preparing di(aryl thiazyl) disulphides which comprises reacting in aqueous solution an alkali metal salt of a 1-mercapto aryl thiazole with ammonium persulphate.

5. The process of preparing di(aryl thiazyl) disulphides which comprises reacting a 1-mercapto aryl thiazole with an oxidizing agent selected from the group consisting of the persulphates, permanganates and perchlorates.

6. The process of preparing di(aryl thiazyl) disulphides which comprises reacting a 1-mercapto aryl thiazole with an oxidizing agent selected from the group consisting of the persulphates, permanganates and perchlorates, acidulating the mass and segregating the resulting di(aryl thiazyl) disulphide.

7. The process of preparing dibenzothiazyl disulphide which comprises interacting aqueous solutions of ammonium persulphate and sodium benzothiazyl mercaptide.

8. The process of preparing a dibenzothiazyl disulphide which comprises reacting, in a liquid medium, a 1-mercaptobenzothiazole with a persulphate.

9. The process of preparing dibenzothiazyl disulphide which comprises reacting an aqueous solution of a salt of 1-mercaptobenzothiazole with a persulphate.

10. The process of preparing a dibenzothiazyl disulphide which comprises reacting, in a liquid

medium, a 1-mercapto-benzothiazole with a permanganate and an acidulating agent.

11. The process of preparing a dibenzothiazyl disulphide which comprises reacting, in a liquid medium, a 1-mercapto-benzothiazole with a perchlorate and an acidulating agent.

12. The process of preparing dibenzothiazyl disulphide which comprises reacting an aqueous solution of a salt of 1-mercaptobenzothiazole with an oxidizing agent selected from the group consisting of the persulphates, permanganates and perchlorates, and acidulating the mass.

13. The process of preparing a di(aryl thiazyl) disulphide which comprises treating a liquid solution of a 1-mercapto aryl thiazole with an oxidizing agent selected from the group consisting of the persulphates, permanganates and perchlorates, and acidulating the mass.

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