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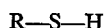
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PROCESS FOR PRODUCING ORGANIC SULFIDES FROM THE REACTION OF MERCAPTANS WITH ALCOHOLS**Robert A. Dombro, Chicago, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware****No Drawing. Filed Oct. 12, 1966, Ser. No. 586,032****Int. Cl. C07c 149/26, 149/32, 149/30****U.S. Cl. 260-609****9 Claims****ABSTRACT OF THE DISCLOSURE**

Organic sulfides can be prepared by reacting a mercaptan, such as n-octyl mercaptan, with an alcohol, such as methanol, in an alkaline medium. The process is useful in removing mercaptans from petroleum products.

This invention relates to a process for the production of organic sulfides and particularly to a process for converting sulfur-containing organic compounds to organic sulfides of the type hereinafter set forth in greater detail.

It has now been discovered that certain sulfur-containing compounds and particularly mercaptans can be converted to sulfides utilizing an alcohol in the presence of an alkaline compound. Therefore, the process will find a particular applicability in removing contaminants from petroleum products. For example, many petroleum products such as hydrocarbons which may be termed as heavy hydrocarbons (those hydrocarbons having a boiling point higher than gasoline) such as kerosene, jet fuel, diesel oil, stove oil, range oil, burner oil, gas oil, fuel oil, etc., as well as hydrocarbons boiling within the gasoline boiling range contain certain contaminants which may have an adverse effect on the use thereof. These contaminants will include mercaptans which possess the generic formula:

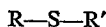


the R comprising an alkyl, aryl, alkaryl, aralkyl radicals. In order to avoid the possibility of the petroleum product becoming gummy from an extended period of storage or other deleterious reactions it is necessary to remove these mercaptans by utilizing the process of the present invention. These mercaptans can be converted to organic sulfides which also easily removable from the petroleum product.

It is therefore an object of this invention to provide a process for preparing organic sulfides.

Another object of this invention is to provide a process for converting mercaptans to organic sulfides.

In one aspect, an embodiment of this invention resides in a process for the production of an organic sulfide having the formula:



in which R and R' are hydrocarbyl selected from the group consisting of alkyl, aryl, alkaryl, aralkyl and cycloalkyl radicals or substituted alkyl, aryl, alkaryl, aralkyl and cycloalkyl radicals which comprises treating a mercaptan with an alcohol at reaction conditions in an alkaline medium, and recovering the resultant organic sulfide.

A specific embodiment of this invention is found in the process for the production of an organic sulfide which comprises treating n-octyl mercaptan with methyl alcohol at a temperature in the range of from about 100° to about 300° C. in the presence of potassium hydroxide and recovering the resultant n-octylmethyl sulfide.

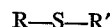
Other objects and embodiments will be found in the following further detailed description of this invention.

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As hereinbefore set forth, the present invention is concerned with a process for converting mercaptans to an organic sulfide. Examples of mercaptans which may undergo the treatment, hereinafter set forth in greater detail, will include alkyl, aryl, alkaryl, aralkyl and cycloalkyl mercaptans such as methyl mercaptan, ethyl mercaptan, propyl mercaptan, isopropyl mercaptan, butyl mercaptan, sec-butyl mercaptan, pentyl mercaptan, n-hexyl mercaptan, n-heptyl mercaptan, n-octyl mercaptan, n-nonyl mercaptan, n-decyl mercaptan and isomers thereof, etc.; phenyl mercaptan, benzyl mercaptan, p-tolyl mercaptan, o-tolyl mercaptan, m-tolyl mercaptan, o-ethylphenyl mercaptan, m-ethylphenyl mercaptan, p-ethylphenyl mercaptan, cyclophenyl mercaptan, cyclohexyl mercaptan, etc., and substituted aryl, alkaryl, aralkyl and cycloalkyl mercaptans where at least one hydrogen on a carbon atom in the mercaptans as stated above is replaced by any radical other than a hydrocarbon radical, such as, for example, halo-, cyano-, sulfonyl, carboxyl, etc., radicals.

The aforementioned mercaptans are treated with an alcohol, the preferred alcohol comprising methyl alcohol, however, it is contemplated that other relatively inexpensive alkyl alcohols such as ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, etc., may also be utilized. The treatment with the alcohol is effected in an alkaline medium such as solutions of potassium hydroxide, sodium hydroxide, lithium hydroxide, rubidium hydroxide, cesium hydroxide, in the alcohol which is here used as both a reactant and a solvent. The sodium hydroxide and potassium hydroxide solutions are preferred due to the fact that sodium and potassium are relatively more available with a correspondingly lower cost of the solution and due to their good solubility in the alcohol solvent.

The organic sulfides which are thus prepared by treating the aforementioned mercaptan will possess the generic formula:



in which R is selected from the group consisting of alkyl, aryl, alkaryl, aralkyl, cycloalkyl and substituted alkyl, alkaryl, aralkyl and cycloalkyl radicals. Specific examples of these sulfides include dimethyl sulfide, ethylmethyl sulfide, n-propylmethyl sulfide, isopropylmethyl sulfide, n-butylmethyl sulfide, n-hexylmethyl sulfide, n-octylmethyl sulfide, n-decylmethyl sulfide, diethyl sulfide, n-propylethyl sulfide, isopropylethyl sulfide, n-pentylethyl sulfide, n-heptylethyl sulfide, phenylmethyl sulfide, phenylethyl sulfide, benzylmethyl sulfide, benzylethyl sulfide, p-tolylmethyl sulfide, p-tolyethylethyl sulfide, cyclopentylmethyl sulfide, cyclopentylethyl sulfide, etc., and the above mentioned sulfides where at least one hydrogen on a carbon atom in the sulfide is replaced by any radical other than a hydrocarbon radical such as halo-, cyano-, sulfonyl, carboxyl, etc., radicals. It is to be understood that the aforementioned sulfides are only representative of the compounds which result from the process described herein and that the present invention is not necessarily limited thereto.

The process of this invention may be effected in any suitable manner and may comprise either a batch or continuous type of operation. For example, when a batch type operation is used, a quantity of sulfur-containing compounds such as a mercaptan is placed in an appropriate apparatus such as a glass liner of a rotating autoclave. In addition, the alcohol and alkaline reagent are added to the reactor which is thereafter sealed, pressurized if necessary and heated to the desired temperature. Upon completion of the desired residence time, the autoclave and contents thereof are cooled to room temperature and the reaction product is recovered. This product is then separated from any unreacted starting materials

and alkaline reagent, and thereafter subjected to fractional distillation under reduced pressure whereby, if so desired, the organic sulfide is recovered. It is also contemplated within the scope of this invention that the treatment of the sulfur-containing compound may be effected in a continuous manner of operation. When such a method is used, the sulfur-containing compounds such as mercaptan is continuously charged to a reaction vessel which is maintained at the proper operating temperature. In addition, the alkali and alcohol are continuously charged thereto through separate means. If so desired, the alcohol and alkali may be admixed prior to entry into said reactor and charged thereto in a single stream. Upon completion of the desired residence time, the reactor effluent is continuously withdrawn and is subjected to separation steps whereby any unreacted starting materials and alkaline reagent are separated from the organic sulfide, the latter being charged to storage while the former compounds may be recycled to form a portion of the feed stock.

While the aforementioned paragraphs have been describing the treatment of sulfur-containing compounds such as mercaptans to form organic sulfides, per se, it is also contemplated that petroleum products may be treated in a continual manner of operation utilizing the process described herein to convert the sulfur-containing contaminants such as mercaptans to organic sulfides. For purposes of illustration, a simplified process will be described in which the petroleum product such as kerosene which is contaminated with mercaptans is passed into a reactor containing the alkaline reagent and alcohol solution at temperatures in the range of from about 100° to about 300° C. Upon completion of the desired residence time, the kerosene is separated from the alcoholic alkali solution to a separator wherein the organic sulfides are separated from the kerosene, the latter being then passed to storage.

The following examples are given to illustrate the process of the present invention which, however, are not intended to limit the generally broad scope of the present invention in strict accordance therewith.

Example I

A mixture of 0.25 mole of n-octyl mercaptan, 0.75 mole of potassium hydroxide and 150 cc. of methyl alcohol was placed in the glass liner of a rotating autoclave. The autoclave was pressurized with nitrogen and heated to a temperature and maintained thereat for a period of 5 hours. At the end of this time, the autoclave and contents thereof were cooled to room temperature and 205 g. of product was recovered. This product consisted of an amber two layered liquid plus some caked solid. The alkaline mixture was extracted with pentane, the extracts were dried over potassium carbonate and pentane was removed, there being obtained 40 g. of an amber oil. This amber oil was distilled under reduced pressure, the cut which had a boiling point of 59–61° C. at a pressure of 1.0–1.4 mm. being recovered. This cut was subjected to gas-liquid chromatographic analysis and to nuclear magnetic resonance spectrum analysis which determined the composition of the cut to be n-octylmethyl sulfide.

Example II

In this example, 0.25 mole of n-butyl mercaptan, 0.75 mole of potassium hydroxide and 150 cc. of methyl alcohol are placed in the glass liner of a rotating autoclave which is thereafter sealed, pressurized with nitrogen, and heated to a temperature of about 250° C. for a period of about 5 hours. At the end of this time, the autoclave and contents thereof are allowed to cool to room temperature and the reaction mixture is recovered, the mixture is extracted with pentane, the extracts dried and the pentane removed by vacuum. The oily product is subjected to fractional distillation and the desired organic sulfide comprising n-butyl methyl sulfide is recovered.

Example III

In this example, 0.25 mole of phenyl mercaptan, 0.75 mole of sodium hydroxide and 150 cc. of ethyl alcohol are treated in a manner similar to that set forth in the above Example I. Upon completion of the desired residence time, the autoclave is cooled, opened and the reaction product recovered therefrom. The reaction product is extracted with pentane, the extracts dried over potassium carbonate after which the solvent is removed by conventional means. After distillation of the resultant oil, the desired product comprising phenylethyl sulfide is recovered.

Example IV

A mixture of cyclopentyl mercaptan, potassium hydroxide and methyl alcohol is placed in a rotating autoclave which is sealed, pressurized with nitrogen, and heated to a temperature of 250° C. The temperature of the autoclave is maintained at this level for a period of 5 hours, following which the autoclave and contents thereof are allowed to cool to room temperature. The autoclave is opened and the reaction product is extracted with n-pentane. After extraction, the resultant mixture is dried and pentane removed by vacuum. Distillation under reduced pressure of the oil will permit the recovery of the organic sulfide which comprises cyclopentylmethyl sulfide.

Example V

A mixture of benzyl mercaptan, sodium hydroxide and ethyl alcohol is treated in a manner similar to that set forth in the above examples, that is, by heating in a rotating autoclave at a temperature of 250° C. under nitrogen pressure for a period of about 5 hours. Upon completion of the residence time, the reaction product which is recovered after venting of the autoclave is extracted using n-pentane as a solvent. The dissolved product is dried over potassium carbonate and the solvent is removed by vacuum. Fractional distillation of the product under reduced pressure will permit the recovery of the resultant benzylethyl sulfide.

Example VI

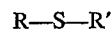
A mixture of kerosene containing 750 p.p.m. sulfur as thiol, methyl alcohol, and potassium hydroxide is treated in a manner similar to that set forth in the above examples, that is, by heating under nitrogen pressure in a rotating autoclave at a temperature of 250° C. for a period of about 5 hours. The recovered kerosene was improved in the following way by said treatment: the color was changed from yellow to almost colorless; the p.p.m. sulfur was reduced to 37 p.p.m.

Example VII

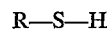
Treatment of alpha-mercaptoacetic acid, 4-dimethylamino thiophenol, 3-cyanocyclopentyl mercaptan, or 4-acetylbenzyl mercaptan in a manner similar to that set forth in the above examples, that is, by heating in a rotating autoclave at a temperature of 250° C. under nitrogen pressure for a period of about 5 hours, produced upon completion of the residence time and subsequent conventional work-up, alpha-methylthioacetic acid, 4-dimethylaminophenylmethyl sulfide, 3-cyanocyclopentylmethyl sulfide, or 4-acetylbenzylmethyl sulfide respectively.

I claim as my invention:

1. A process for the production of an organic sulfide having the formula:



in which R and R' are hydrocarbyl radicals which comprises treating a mercaptan having the formula



where R is as defined above, with an alcohol having the formula



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where R' is as defined above at reaction conditions including a temperature in the range of from about 100° to about 300° C. in the presence of an alkali metal hydroxide.

2. The process as set forth in claim 1, further characterized in that said alkaline medium comprises a potassium hydroxide solution.

3. The process as set forth in claim 1, further characterized in that said alcohol is methyl alcohol.

4. The process as set forth in claim 3, further characterized in that said mercaptan is n-butyl mercaptan and the resultant organic sulfide is n-butylmethyl sulfide.

5. The process as set forth in claim 3, further characterized in that said mercaptan is n-octyl mercaptan and said resultant organic sulfide is n-octylmethyl sulfide.

6. The process as set forth in claim 3, further characterized in that said mercaptan is cyclopentyl mercaptan and said resultant organic sulfide is cyclopentylmethyl sulfide.

7. The process as set forth in claim 1, further characterized in that said alcohol is ethyl alcohol.

8. The process as set forth in claim 7, further char-

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acterized in that said mercaptan is phenyl mercaptan and said resultant organic sulfide is phenylethyl sulfide.

9. The process as set forth in claim 7, further characterized in that said mercaptan is benzyl mercaptan and said resultant organic sulfide is benzylethyl sulfide.

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15 CHARLES B. PARKER, *Primary Examiner*.

D. R. PHILLIPS, *Assistant Examiner*.

U.S. Cl. X.R.

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