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PROCESS FOR MAKING NEUTRAL HYDROXY SUBSTITUTED TRIESTERS OF PHOSPHORODITHIOIC ACID

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13 Claims. (Cl. 260—978)

This invention relates to the chemistry or organo phosphorus compounds and more particularly, to the chemistry of phosphorodithioic acids. Still more particularly it relates to a process whereby these acids are converted to neutral hydroxy-substituted triesters of phosphorodithioic acids.

The development trend in petroleum lubricating oils has been toward the use of more efficient refining methods to reduce the sludging tendency of such oils. However, these highly refined oils have decreased resistance to oxidation and are more likely to form soluble acidic oxidation products which are corrosive, particularly under severe service conditions. Although generally superior to lightly refined oils they may form a "varnish" film on hot metal surfaces, such as the cylinder walls and pistons of an internal combustion engine, under very severe engine operating conditions.

This invention is a process for making products which can be formulated with highly refined petroleum fractions to give improved motor oils and gear lubricants. In such formulation, the products of this process serve both as corrosion inhibitors and also as extreme pressure agents. For example, the addition of small proportions of the products of this process to a refined lubricating oil greatly reduces the tendency of such oil to corrode metal surfaces, especially those of copper-lead and silver-lead bearings. In addition, gear lubricants which are subjected to extreme pressure conditions are greatly improved by the addition of the products of this process so that they may better withstand the extreme pressures of the environments in which they are used.

In addition to the desirability of these products as corrosion inhibitors and as extreme pressure agents, they are particularly useful in lubricating formulations because of their compatibility with other known lubricant additives.

Furthermore, these products are useful as ore floatation agents and as metal finishing agents. They are also valuable as starting materials for the preparation of still other effective lubricant additives.

It is a principal object of the invention to provide a novel process for the preparation of certain lubricant additives and lubricant additive intermediates.

It is also an object of the invention to provide a convenient process for the preparation of neutral phosphorus- and sulfur-containing compositions.

These and other objects are accomplished by the process which comprises the reaction of a salt of a phosphorodithioic acid having the following structure.

$$(RO)_2PSSH \cdot NR'_3$$

where R is a hydrocarbon radical and R′ is selected from the class consisting of hydrogen and hydrocarbon radicals with at least about an equivalent amount of an organic compound selected from the class consisting of epoxides and thioepoxides. The product of this reaction is a hydroxy-substituted triester or mercapto-substituted triester, as the case may be.

The hydrocarbon radicals of the above structure may be aliphatic or aromatic and may contain organic or inorganic substituents. The term "hydrocarbon" includes not only those radicals which are wholly hydrocarbon but also those which despite the presence of one or more

non-hydrocarbon substituents still retain their substantially hydrocarbon character. Illustrative types of organic radicals include alkyl, cycloalkyl, aryl, aralkyl, alkaryl, alkenyl, cycloalkenyl, etc., and the substituted derivatives of these, e.g., nitro, halo, alkoxy, hydroxy, carboxy, etc. Generally these organic radicals are hydrocarbon radicals.

The phosphorodithioic acids from which the hydroxy-substituted triesters can be derived are well known. They may be prepared by the reaction of phosphorus pentasulfide with a hydroxy compound which corresponds to the organic radical R. This reaction is illustrated by the action of phosphorus pentasulfide on ethyl alcohol to produce O,O′-diethylphosphorodithioic acid. In similar fashion, aliphatic hydroxy compounds such as propyl, butyl, isobutyl, amyl, hexyl, cyclohexyl, n-octyl, iso-octyl, lauryl, etc., alcohols or aromatic hydroxy compounds such as phenol, alkylated phenols, naphthols, alkylated naphthols, and the like may be reacted with phosphorus pentasulfide to produce phosphorodithioic acids of utility as starting materials for the present invention.

The reaction of phosphorus pentasulfide with a mixture of alcohols or phenols (e.g., isobutanol and n-hexanol in 2:1 weight ratios) results in phosphorodithioic acids in which the two organic radicals are different. Such acids likewise are useful herein.

The ammonium salt of phosphorodithioic acid is prepared by passing an equivalent amount of ammonia gas into the acid or a solution of the acid in an inert solvent to obtain the neutral salt. Similarly, the amine salt of a phosphorodithioic acid is prepared by adding an equivalent amount of an amine to the acid or a solution of the acid.

The amines useful for forming the phosphorodithioic acid salts of this invention may be aliphastic amines, aromatic amines, or cyclo-aliphatic amines. Amines having from 1 to about 15 aliphatic carbon atoms are preferred. Methyl amine, ethyl amine, n-propyl amine, isopropyl amine, n-butyl amine, isobutyl amine, secondary butyl amine, tertiary butyl amine, n-amyl amine, isoamyl amine, n-heptyl amine, n-hexyl amine, octyl amine, nonyl amine, decyl amine, hendecyl amine, dodecyl amine, tridecyl amine, tetradecyl amine, pentadecyl amine, dimethyl amine, diethyl amine, di-n-propyl amine diisopropyl amine, dibutyl amine, diamyl amine, dihexyl amine, trimethyl amine, triethyl amine, benzyl amine, pyridine, morpholine, ethylene diamine, piperazine, cyclopentyl amine, and diethylene triamine are specific examples of useful amines.

The reaction of a phosphorodithioic acid with ammonia is exothermic and may be carried out at temperatures within the range from about −35° C. to the decomposition temperature of the salt, or about 200° C. It is the usual procedure to start passing ammonia into the acid at about 20°–60° C. and to allow the temperature to rise at about 90°–100° C., keeping the temperature of the reaction at about 100° C. by controlling the rate of ammonia addition and by external cooling if necessary.

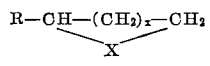
Most of the amine and ammonium phosphorodithioates are crystalline solids at room temperature. This property affords the distinct advantage of being able to purify the amine phosphorodithioates by recrystallization from a suitable solvent before further reaction, and thus to obtain a very pure hydroxy-substituted triester.

The reaction of the amine and ammonium phosphorodithioate salt with an epoxide is also somewhat exothermic. It is easily controlled by the rate of addition of the epoxide. Although it is not necessary, it is preferred to control the temperature of the reaction mixture so that it is reasonably constant throughout the course of the reaction. The temperature of the reaction may be as low as −60° C. or lower, and on the other hand, it may

be as high as 200° C. or even higher. Generally, for reasons of economy, it is preferred to carry out the process at a sufficiently high temperture such that the amine salt of the phosphorodithioic acid is liquid rather than to react the epoxide with a solution of the amine salt at a lower temperature.

Removal of the amine from the product can be effected, if desired by blowing with nitrogen or other inert gas or by applying reduced pressure (if the amine is volatile). Removal of higher boiling amines requires correspondingly more drastic treatment.

The organic epoxides and thioepoxides may be represented by the structural formula



where R is a hydrocarbon radical or hydrogen, X is sulfur or oxygen, and *n* is 1 or 0. Those epoxides and thioepoxides are preferred in which one of the carbon atoms attached to oxygen or sulfur is also attached to two hydrogen atoms. In other words, the preferred epoxides and thioepoxides are terminal epoxides. These have been given the name terminal epoxides and thioepoxides because they may be thought of as being derived in most instances, from a vinyl compound which has a terminal olefinic double bond.

The reaction appears to involve equimolar proportions of the amine or ammonium salt of the phosphorodithioic acid and the epoxide. This reaction appears to be unique in that ammonia or the amine is liberated upon addition of an epoxide. Since ammonia and amines are basic compounds it would not be expected that they would be liberated from their salts by a neutral material such as propylene oxide. The identity of the products have not been established other than that they are known to be hydroxy-substituted triesters and so they are best described in terms of their method of preparation. The products are neutral, having a phosphorus to sulfur ratio of 1:2, and as indicated before, appear to result from the reaction of one mole each of amine or ammonium phosphorodithioate and epoxide.

It is usually convenient to use an excessive amount of the organic epoxide so as to insure a maximum yield. In most instances the epoxide is sufficiently volatile that its removal from the reaction mixture, after the reaction is finished, is a simple operation. In some cases, it is sufficient merely to allow the excess epoxide to evaporate from the product at room temperature, or the product may be flushed with an inert gas such as nitrogen, or subjected to reduced pressure.

The process of the invention is illustrated further in detail by the following specific examples:

Example 1

Dry nitrogen gas is passed through a solution of 2640 grams (8 equivalents) of O,O'-di-(2-methylpentyl-4) phosphorodithioic acid in 600 grams of toluene for 15 minutes and then 146 grams (8.6 equivalents) of ammonia gas is passed into the solution, over a period of 2.2 hours, the temperature rising from room temperature to 65° C. Dry nitrogen gas is passed through the solution for 5 minutes to remove excess ammonia whereupon 510 grams (8.8 equivalents) of propylene oxide is added at 50° to 43° C. with cooling over a period of two hours. The reaction mixture is stirred for one hour to assure complete reaction, and then heated to 80° C. over a two hour period at 100 mm. mercury pressure. The residue is the product. The product has the following analysis: P, 8.44%; S, 17.77%; N, 0.136%; OH, 5.00%, neut. no. (to bromophenol blue), 3.79 acid. Yield, 3131 grams.

Example 2

Nitrogen gas is passed through 1320 grams (4 equivalents) of O,O'-di-(2-methylpentyl-4) phosphorodithioic acid for 15 minutes at a room temperature, followed by 68 grams (4 equivalents) of ammonia gas at 28°–96° C.

for 1.5 hours. Propylene oxide (255 grams, 4.4 equivalents) is added over a three hour period at 95°–45° C. and the mixture is stirred for an additional 0.5 hour to assure complete reaction, heated to 85° C., and stripped to 85° C./100 mm. The product is cooled at 60° C. and an additional 40 grams (0.7 equivalent) of propylene oxide is introduced beneath the surface. Stirring is continued for one hour at 55°–60° C. followed by heating to 85° C. under a vacuum of 100 mm. The resulting product has the following analysis: P, 8.21%; S, 16.25%; N, 0.444%; OH, 4.85%; yield, 1512 grams.

Example 3

To 330 grams (1.0 equivalent) of O,O'-di-(2-methylpentyl-4) phosphorodithioic acid, 196 grams (1.02 equivalents) of a commercial aliphatic primary amine having an average molecular weight of 191 in which the aliphatic radical is a mixture of tertiary-alkyl radicals containing from 11 to 14 carbon atoms, is added over a one hour period during which the temperature rises from room temperature to 65° C. To the thus formed salt, 64 grams (1.1 equivalents) of propylene oxide is added at room temperature to 45° C. over a 2.5 hour period. The reaction mixture is heated at 75°–80° C. for two hours and then vacuum stripped to 80° C./20 mm. The product has the following analysis: P, 5.5%; S, 10.09%; N, 2.52%; yield, 558 grams.

Example 4

Dry nitrogen gas is passed for 30 minutes through a phosphorodithioic acid prepared by reacting four moles of a mixture of 65% isobutanol and 35% primary amyl alcohol with one mole of phosphorus pentasulfide. 68 grams (4.0 equivalents) of ammonia gas is passed into 1108 grams (4.0 equivalents) of this phosphorodithioic acid, the temperature rising from 30° C. to 93° C. The resulting salt is heated to 105° C. and 255 grams (4.4 equivalents) of propylene oxide is added over a three hour period at 105°–55° C. The reaction mixture is stirred for one hour at 50° C., heated to 85° C. for 15 minutes, and then stripped at 85° C./100 mm. Twenty grams of a commercial diatomaceous earth filter aid is added and the product is filtered while hot. The filtrate is the product and had the following analysis: S, 17.49%; P, 10.7%; N, 3.30%; OH, 3.51%; yield, 1109 grams.

Example 5

To 1320 grams (4.0 equivalents) of O,O'-di-(2-methylpentyl-4) phosphorodithioic acid at 28°–96° C. There is added 68 grams (4.0 equivalents) of ammonia gas over a period of 1.5 hours. 1 - butene oxide (316 grams, 4.4 equivalents) is added to the resulting salt at 95°–45° C. over a three hour period. The reaction mixture is stirred for one-half hour, heated to 85° C., and stripped at 85° C./100 mm. The residue is the product.

Example 6

Propyl amine (236 grams, 4.0 equivalents) is added to 1320 grams (4.0 equivalents) of O,O'-di-(2-methylpentyl-4) phosphorodithioic acid throughout a period of 1.2 hours, at 28°–102° C. Propylene oxide (255 grams, 4.4 equivalents) is added to the resulting salt at 100°–50° C. throughout a three hour period. The reaction mixture is stirred for one-half hour and then heated to 85° C. The product is stripped to a temperature of 85° C./20 mm. to recover liberated propyl amine. The residue is the product.

Example 7

Dimethyl amine (180 grams, 4.0 equivalents) is passed into 1320 grams (4.0 equivalents) of O,O'-di-(2-methylpentyl-4) phosphorodithioic acid during a 1.5 hour period at 28°–95° C. To the resulting amine salt there is added 255 grams (4.4 equivalents) of propylene oxide over a three hour period at 95°–45° C. Stirring is continued for one-half hour, and then the reaction mixture is heated to

85° C. and stripped at 85° C./20 mm. The residue is the product.

Example 8

Ammonia gas (68 grams, 4.0 equivalents) is passed into 1320 grams (4.0 equivalents) of O,O'-di-(2-methylpentyl-4) phosphorodithioic acid throughout a period of 1.25 hours, at 25° C.–95° C. Ethylene oxide (176 grams, 4.0 equivalents) is introduced beneath the surface of the resulting salt throughout a three hour period, at 95°–45° C. The reaction mixture is stirred an additional one-half hour, heated to 85° C., and stripped at 95° C./20 mm. The residue is the product.

Example 9

Pyridine (316 grams, 4.0 equivalents) is added to 1,320 grams (4.0 equivalents) of O,O'-di-(2-methylpentyl-4) phosphorodithioic acid during a 1.25 hour period at 25°–99° C. Propylene oxide (464 grams, 8.0 equivalents) is added to the salt over a 2.5 hour period at 95°–45° C. The reaction mixture is stirred an additional one-half hour, heated to 85° C. and stripped to 85° C./50 mm. The residue is the product.

Example 10

Ammonia gas (34 grams, 2.0 equivalents) is passed into 708 grams (2.0 equivalents) of O,O'-di-iso-octyl phosphorodithioic acid in one hour at 25°–75° C. Propylene oxide (348 grams, 6.0 equivalents) is introduced beneath the surface of the resulting salt in two hours at 95°–45° C. The reaction mixture is stirred an additional one-half hour, heated to 85° C. and stripped to 85° C./100 mm. The residue is the product.

Example 11

Into 588 grams (2.0 equivalents) of O,O'-di-cyclohexyl phosphorodithioic acid, 34 grams (2.0 equivalents) of ammonia gas is introduced in one-half hour at 25°–95° C. To this salt, 128 grams (2.2 equivalents) of propylene oxides is introduced in 1.5 hours at 95°–50° C. The product mixture is stirred an additional one-half hour, heated to 85° C., and stripped to 85° C./100 mm. The residue is the product.

Example 12

Ammonia gas (34 grams, 2.0 equivalents) is passed into 257 grams (2.0 equivalents) of O,O'-di-2-chlorophenyl phosphorodithioic acid at room temperature to 85° C. over a one hour period. Propylene oxide (174 grams, 2.2 equivalents) is added over 1.5 hours at 85°–45° C. The reaction mixture is stirred 1 hour at 50° C., heated to 85° C. for 15 minutes and stripped at 85° C./100 mm. The residue is the desired product.

Example 13

Ammonia gas (34 grams, 2.0 equivalents) is passed into 708 grams (2.0 equivalents) of O,O'-di-iso-octyl phosphorodithioic acid at room temperature to 97° C. over 1.25 hours. Ethylene sulfide (132 grams, 2.2 equivalents) is introduced beneath the surface of the ammonium salt at 85°–95° C. over a 1.5 hour period. The reaction mixture is heated an additional one hour at 85° C. and vacuum stripped to 85° C./100 mm. The residue is the product.

A useful derivative of the hydroxy-substituted triesters of phosphorodithioic acids is prepared by the reaction with an inorganic phosphorus reagent selected from the class consisting of phosphorus acids, phosphorus oxides, and phosphorus halides. The preferred inorganic phosphorus reagent in the reaction with the hydroxy-substituted triesters of phosphorodithioic acids is phosphorus pentoxide. The products of this reaction are acidic materials which in themselves are useful.

These acidic materials may be further reacted with basic reacting metal oxides or with amines to make other useful products. These are described more fully in copending application No. 130,270 filed August 9, 1961.

What is claimed is:

1. The process of preparing hydroxy-substituted phosphorodithioic acid triesters which comprises the reaction at a temperature within the range of from about —60° C. to about 200° C. of the ammonium salt of a dialkyl phosphorodithioic acid with at least about an equivalent amount of propylene, with the liberation of ammonia from said salt oxide.

2. The process of preparing hydroxy- or mercapto-substituted phophorodithioic acid triesters which comprises reacting at a temperature within the range of from about —60° C. to about 200° C., a salt of a phosphorodithioic acid having the structural formula

$$(RO)_2PSSH \cdot NR'_3$$

wherein R is hydrocarbon and R' is hydrogen or hydrocarbon with at least about an equivalent amount of a compound selected from the class consisting of epoxy lower alkanes, epoxy lower alkenes, styrene oxide, epichlorohydrin and thioepoxy lower alkanes, with the liberation of NR'_3 from said salt.

3. The process of preparing hydroxy-substituted phosphorodithioic acid triesters which comprises reacting at a temperature within the range of from about —60° to about 200° C., the ammonium salt of a dialkyl phosphorodithioic acid with at least about an equivalent amount of an epoxy lower alkane, with the liberation of ammonia from said salt.

4. The process of preparing hydroxy-substituted phosphorodithioic acid triesters which comprises reacting at a temperature within the range of from about —60° C. to about 200° C., the amine salt of a dialkyl phosphorodithioic acid with at least about an equivalent amount of an epoxy lower alkane, with the liberation of the amine from said salt.

5. The process of preparing hydroxy-substituted phosphorodithioic acid triesters which comprises reacting at a temperature within the range of from about — 60° C. to about 200° C., the ammonium salt of a dialkaryl phosphorodithioic acid with at least about an equivalent amount of an epoxy lower alkane, with the liberation of ammonia from said salt.

6. The process of preparing hydroxy-substituted phosphorodithioic acid triesters which comprises reacting at a temperature within the range of from about —60° C. to about 200° C., the ammonium salt of a dicycloalkyl phosphorodithioic acid with at least about an equivalent amount of an epoxy lower alkane, with the liberation of ammonia from said salt.

7. The process of preparing hydroxy-substituted phosphorodithioic acid triesters which comprises reacting at a temperature within the range of from about —60° C. to about 200° C., the ammonium salt of a dialkyl phosphorodithioic acid with at least about an equivalent amount of epichlorohydrin, with the liberation of ammonia from said salt.

8. The process of preparing hydroxy-substituted phosphorodithioic acid triesters which comprises reacting at a temperature within the range of from about —60° C. to about 200° C., the ammonium salt of a dialkyl phosphorodithioic acid with at least about an equivalent amount of an epoxy lower alkane, wherein each alkyl group of the phosphorodithioic acid has from 3 to 12 carbon atoms, with the liberation of ammonia from said salt.

9. The process of preparing hydroxy-substituted phosphorodithioic acid triesters which comprises reacting at a temperature within the range of from about 40° C. to about 110° C., the ammonium salt of a dialkyl phosphorodithioic acid with at least about an equivalent amount of an epoxy lower alkane, wherein the alkyl groups of the phosphorodithioic acid are different and each has

from 3 to 12 carbon atoms, with the liberation of ammonia from said salt.

10. The process of preparing mercapto-substituted phosphorodithioic acid triesters which comprises reacting at a temperature within the range of from about 40° C. to about 110° C., the ammonium salt of a dialkyl phosphorodithioic acid with at least about an equivalent amount of a thioepoxy lower alkane, with the liberation of ammonia from said salt.

11. The process of preparing hydroxy-substituted phosphorodithioic acid triesters which comprises reacting at a temperature within the range of from about 40° C. to about 110° C., the ammonium salt of an O,O'-di-(2-methylpentyl-4)phosphorodithioic acid with at least about an equivalent amount of propylene, with the liberation of ammonia from said salt oxide.

12. The process of preparing hydroxy-substituted phosphorodithioic acid triesters which comprises reacting at a temperature within the range of from about 40° C. to about 110° C., the ammonium salt of an O,O'-di(2-methylpentyl-4)phosphorodithioic acid with at least about

an equivalent amount of ethylene oxide, with the liberation of ammonia from said salt.

13. The process of preparing hydroxy-substituted phosphorodithioic acid and triesters which comprises reacting at a temperature within the range of from about 40° C. to about 110° C., the ammonium salt of a dialkyl phosphorodithioic acid with at least about an equivalent amount of a propylene oxide in which the dialkyl phosphorodithioic acid is prepared by the reaction of phosphorus pentasulfide with a mixture of aliphatic alcohols, with the liberation of ammonia from said salt.

References Cited by the Examiner

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,284,548 November 8, 1966

Emil T. Wierber

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 10, for "or" read -- of --; column 2, line 35, for "aliphastic" read -- aliphatic --; line 56, for "at" read -- to --; column 3, after line 26, insert the following paragraph:

> Specific examples of suitable epoxides include ethylene oxide, propylene oxide, epichlorohydrin, 1-butene oxide, butadiene monoxide, 1-amylene oxide, styrene oxide, ethylene sulfide, propylene sulfide, etc.

column 4, line 5, for "at" read -- to --; line 49, for "There" read -- there --; column 5, line 75, beginning with "These acidic" strike out all to and including "August 9, 1961", in column 6, line 3; column 6, line 10, and column 7, line 15, after "propylene", each occurrence, insert -- oxide --; column 6, line 11, and column 7, line 16, strike out "oxide", each occurrence.

Signed and sealed this 28th day of November 1967.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents