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ESTERS OF ALKANEDIPHOSPHONIC ACIDS

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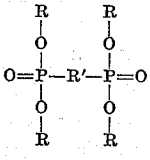
No Drawing. Filed Feb. 26, 1958, Ser. No. 717,548

4 Claims. (Cl. 260—461)

This invention pertains to certain novel esters of alkanediphosphonic acids. More particularly, this invention pertains to neutral esters of certain alkanediphosphonic acids and certain alkanols.

I have discovered a new class of phosphorus esters which are highly suitable as components of hydraulic fluids. This new class of compounds consists of the neutral esters of alkanediphosphonic acids of from three to ten carbon atoms and alkanols of from three to nine carbon atoms, the said neutral esters containing at least nineteen carbon atoms. I have found that these particular esters themselves are excellent hydraulic fluids, and that they impart highly desirable properties to hydraulic fluid compositions of which they are a part. These new esters are substantially non-corrosive and are outstandingly resistant to both oxidation and thermal degradation over a wide range of conditions. Further, these esters have been found to have very low pour points (below minus 65° F.), which permits their use in hydraulic fluids which encounter very low temperatures. This property of the new esters is wholly unexpected, since the neutral alkyl esters of the next lower molecular weight homologous alkanediphosphonic acid (ethanediphosphonic acid (containing two carbon atoms)) have markedly higher pour points, as is evidenced by the fact that the pour point of the tetrabutyl ester of ethanediphosphonic acid has a pour point of plus 60° F., or more than 125° F. above the pour points of the new esters. My discoveries thus provide a new class of hydraulic fluids which are useful over an unusually wide range of temperatures.

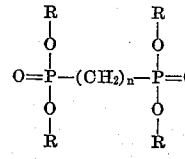
The phosphorus esters of this invention are characterized by the configuration:



wherein each of the groups designated by the symbol R (which groups may be the same or different) is an alkyl group of from three to nine carbon atoms, and the group designated by the symbol R′ is an alkylene group, preferably an alpha,omega-alkylene group, of from 3 to 10 carbon atoms, and preferably from 3 to 6 carbon atoms. It is preferred that at least two of the groups designated by the symbol R are of branched-chain configuration. The esters must each contain a total of at least 19 carbon atoms.

The esters of this invention thus are generically termed neutral esters of alkanediphosphonic acids of from 3 to 10 (preferably 3 to 6) carbon atoms and alkanols of from 3 to 9 carbon atoms, the esters containing at least 19 carbon atoms. The esters of this invention may also be characterized as bis(dialkyl phosphono)alkanes, and as tetraalkyl alkanediphosphonates with appropriate restriction of the number of carbon atoms on each of the alkyl and alkane groups.

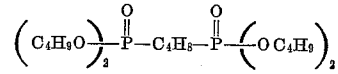
The preferred esters of this invention are characterized by the configuration:



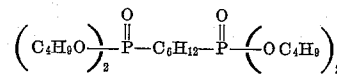
wherein R has the meaning set out hereinbefore and n is an integer of from 3 to 10, and preferably from 3 to 6.

The following compounds are exemplary of this invention and the structure of the new compounds provided thereby:

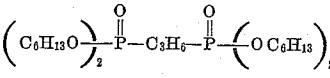
(*a*) Bis-1,4-(dibutyl phosphono)butane:



(*b*) Bis-1,6-(dibutyl phosphono)hexane:



(*c*) Bis-1,3-(di-n-hexyl phosphono)propane:



Other examples of the novel compounds are:

Bis-1,3-(diisobutyl phosphono)propane
Bis-1,8-(diisopropyl phosphono)octane
Bis-1,5-(di(2-ethylhexyl)phosphono)pentane
Bis-1,6-(di(3-methylbutyl)phosphono)hexane
1-(dibutyl phosphono)-6-(dioctyl phosphono)hexane
Bis-1,3-(di(3,5,5-trimethylhexyl)phosphono)propane
Bis-1,3-(di(2-ethylbutyl)phosphono)propane
1-(diisopropyl phosphono)-5-(dibutyl phosphono)pentane

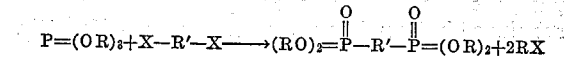
The alkylene group separating the two phosphono radicals may be of branched-chain configuration as typified by the following compounds:

Bis-1,2-(di-tert-butyl phosphono)-3,4-dimethylpentane
Bis-2,4-(di-sec-butyl phosphono)-3,5-dimethylhexane
Bis-1,6-(di-n-pentyl phosphono)-3,4,5-trimethylhexane

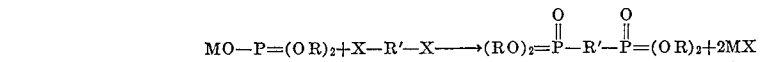
It will be understood that the invention is not limited to symmetrical compounds. For example, the various substituents denoted as R in the above general formula may vary within a given compound, both with respect to carbon atom content and spatial configuration. The branched configurations are favored due to their generally superior effect upon the lubricating characteristics, especially at low temperatures. Additionally, while the two end groups may be identical in a single compound for specific purposes, it is sometimes desirable to include two different types of phosphorus end groups in order to obtain the beneficial properties attributable to each type.

The compounds of the invention may be prepared by the reaction of an alkane dihalide with (*a*) a trialkyl phosphite or (*b*) an alkali metal salt of a dialkyl phosphite or (*c*) they may be prepared by the reaction of an alkalinous metal salt of a diester of phosphorous acid with an ester of a carboxylic acid.

In case (*a*), the general reaction is:

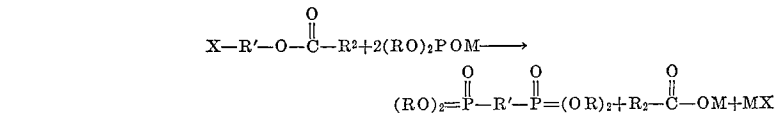


In case (*b*), the general reaction is:

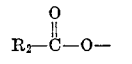


in which equations, R and R′ have the definitions already given to them, X=a halogen atom and M=an alkali metal atom.

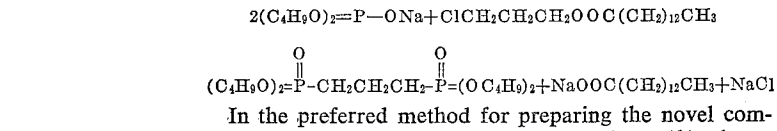
In case (*c*) the general reaction is:



where R^2 is an alkyl group and the other symbols have the definition given above. It is preferred that the group



be the residue of a fatty acid. This reaction is exemplified by the reaction of sodium dibutyl phosphite with 3-chloropropyl myristate according to the reaction:



In the preferred method for preparing the novel compounds of the invention according to (*a*) or (*b*) above, the phosphite is dissolved in a suitable neutral solvent, such as toluene or xylene, which is not reactive with the other components of the reaction mixture. To this solution over a substantial period of time is added the alkane dihalide. This mixture is stirred during the addition of the dihalide and then is refluxed at atmospheric pressure within the temperature range of from about 50° C. to about 150° C. until the desired product has been formed.

Though the reaction is normally substantially complete in about 10 hours, somewhat longer or shorter periods of refluxing can be employed without deleterious results. In general it has been found that the desired degree of reaction is obtained in from about 4 to about 16 hours.

An alternative method of procedure, which has been found to be very effective in many cases is the following: reflux an alkali metal—preferably sodium—in a suitable solvent such as heptane while a dialkyl phosphite is added slowly, then reflux for a period of from 1 to 4 hours to form an alkali metal dialkyl phosphite. Then gradually add a dihaloalkane—preferably a dibromoalkane—to the refluxing solution. After heating from about 1 to about 8 hours at reflux, the corresponding bis-(dialkyl phosphono)alkane has been formed.

Where the phosphorus ester employed contains no alkali metal, upon commencement of the reaction and while the reaction is in progress, an organic halide, formed by the union of an alkyl radical of the phosphorus reactant with the halogen of the alkane dihalide, is evolved. Such organic halide advantageously is continuously volatilized from the reaction mixture and withdrawn from the system as formed, as by conducting the reaction at boiling in a vessel equipped with a fractionating column and continuously fractionating the evolved organic halide from the vapors. The extent of the reaction may be followed by collecting and measuring the amount of the evolved organic halide. Ordinarily the heating will be continued until reaction ceases, as judged by the cessation of the evolution of the organic halide; the reaction, of course, may be interrupted at an earlier time if desired.

At the end of the refluxing period, the reaction mixture is cooled to room temperature. The subsequent procedure then depends upon the type of reactants employed.

(1) When the initial phosphorus reactant is a trialkyl phosphite, the mixture following reaction contains the substituted hydrocarbon and some organic halide. These

products are separated by distillation and the crude substituted hydrocarbon purified as indicated below.

(2) When the initial phosphorus reactant is an alkali metal salt of a dialkyl phosphite, the mixture following reaction contains the substituted hydrocarbon and an alkali metal halide. The alkali metal halide is filtered off and the remaining solution is water-washed, neutralized with dilute alkali, water-washed again and the volatile diluent removed by topping to a temperature of about 150° C. at 150 mm. pressure. If a highly purified product is desired the bottoms from this topping may then be distilled in a molecular still to obtain purified product as distillate.

If method (*c*) above is employed, the reaction may be carried out by heating a mixture comprising the salt of the diester of phosphorous acid and the ester of the carboxylic acid at an elevated temperature that is conducive to the reaction but that is below a temperature which would cause excessive occurrence of decomposition, side reactions and the like. A broad range of temperature in carrying out the reaction is from about 50° C. to about 250° C., but in most cases the optimum temperature will be between about 100° C. and about 200° C. The reaction may be carried out in the presence of inert organic solvents such as are described below. The amount of solvent is not critical, within the broad limits outlined below. In carrying out the reaction, the reactants may be heated in any suitable reaction vessel until the desired reaction has occurred. The reactants are preferably present in the reaction theatre in about the theoretically required amounts. The pressure may be atmospheric, subatmospheric or superatmospheric, as desired. When the boiling points of the reactants and product are such that undue loss through volatilization cannot occur, the reaction frequently may be conducted most simply by heating the mixture in a vessel open to the atmosphere, under a blanket of inert gas, such as nitrogen, if desirable, or the reaction may be carried out at atmospheric pressure in a vessel equipped for reflux. Recovery of the product and its purification follows the procedure states for methods (*a*) and (*b*) above.

Whatever method is employed for forming the compounds of the present invention, there should be employed from about 0.5 to about 5.0 gram-moles of the phosphite per gram-atom of halogen present in the reaction theatre. As long as these reaction proportions are employed, the concentration of the reactants in the solvent-reaction solution may be varied within relatively wide limits. The practical limits of the concentration of the reactants in the solvent are determined by the relative solubility of the initial reactants and the reaction products in the particular solvent employed.

The solvent used may be any solvent which satisfies the following requirements:

(*a*) It must be inert as to the reactants and the reaction products.

(*b*) All the reactants and reaction products must be soluble in some substantial degree in the solvent, with the exception of the alkali metal halide, if such be formed by the reaction.

Typical examples of the solvent which may be used include: toluene, xylene, Cellosolve, Hi-Flash naphtha, petroleum ethers and the like.

The phosphorus compounds which may be used to prepare the compounds of the invention are the neutral alkyl esters of phosphorous acid and the alkali metal salts thereof. These compounds may be represented by the general formulae:

(I) Trialkyl phosphite, $P(OR)_3$;
(II) Alkali metal dialkyl phosphites $MO—P(OR)_2$;

in which formulae R has the definition already given and and M is an alkali metal atom.

In these trialkyl phosphites, the alkyl groups may be the same or dissimilar. The alkyl groups may be straight-

chain or branched-chain in configuration. Suitable trialkyl phosphites which may be employed include, among others, tributyl phosphite, tri-isopropyl phosphite, tri-n-propyl phosphite, tri-(3-methylhexyl)phosphite, tri-(2-ethylhexyl)phosphite, tri - (3,5,5-trimethylhexyl)phosphite, tri-(tert-butyl)phosphite, tri-(sec-butyl)phosphite and tri-(n-pentyl)-phosphite.

Instead of a trialkyl phosphite, there may be employed the alkali metal salts of dialkyl phosphites. Suitable alkali metal dialkyl phosphites include, among others, the sodium and potassium salts of the trialkyl phosphites above.

The alkane dihalides which may be used to prepare the compounds of the present invention are the alpha,omega-dihaloalkanes, having the general formula:

$$X—R'—X$$

wherein X is a halogen atom and R' is an alpha,omega-alkylene radical of either straight-chain or branched-chain configuration. Of the halogens, bromine is preferred. Representative compounds of this reactant are, among others, 1,4-dibromobutane, 1,3-dichloropropane, 1,6-dibromo-3,4,5-trimethylhexane, 1,2-dibromo-3,5-dimethylhexane, and the like.

The ester of the carboxylic acid which may be used to prepare the compounds of the invention according to method (*c*) have the general configuration:

$$X—R'—O—\overset{\overset{O}{\|}}{C}—R^2$$

where R', X and R^2 have the definitions given above. It is preferred that the group

$$R^2—\overset{\overset{O}{\|}}{C}—O—$$

be the residue of a fatty acid containing from 3 to 26 carbon atoms.

These compounds are characterized by the fact that the ester group is substituted on the omega carbon atom by a halogen atom. Examples of this group, among others, are: 4-chlorobutyl myristate and gamma-bromopropyl adipate.

The following examples illustrate the preparation of compounds of this invention and the table included in the last example presents typical properties of the diphosphorus derivatives, indicating their suitability for use as hydraulic fluids.

EXAMPLE I

Preparation of bis-1,4-(dibutyl phosphono)butane: 330 grams (1.7 moles) of redistilled dibutyl phosphite was added gradually to 39 grams (1.7 moles) of sodium in about 2000 milliliters of refluxing heptane. After all the phosphite had been added, the mixture was allowed to reflux for two hours to allow the reaction to be completed. At the end of this period 160 grams (0.85 mole) of tetramethyl dibromide (boiling point 196–197° C.) was added gradually to the refluxing solution. Heating and stirring were continued for three hours to complete the reaction and to coagulate the sodium bromide. The salt was then removed by filtration and the colorless filtrate washed with water until neutral washings were obtained (first washings were slightly alkaline, presumably due to some unreacted sodium dibutyl phosphonate) and then topped to 150° C. kettle temperature at 150 millimeters pressure to remove the n-heptane solvent and water. The residue was then distilled in a falling film molecular still at 132° C. and 1×10^{-5} millimeters pressure. The distillate was clear and colorless and had an acid number of 0.07 milligram of KOH/gram of sample. The yield was 238 grams, which is 63.5% of theoretical.

EXAMPLE II

Preparation of bis-1,6-(dibutyl phosphono)hexane: 826 grams (4.25 moles) of dibutyl phosphite were added to 1500 grams of toluene and the mixture was stirred and

warmed to 37° C. 92 grams (4 moles) of sodium metal were added to the thoroughly agitated mixture over a period of 50 minutes, the temperature rising to 112° C. This mixture was refluxed at 112° C. for 3½ hours. At the end of this time, addition of hexamethylene dibromide to the reaction mixture was begun. 488 grams (2 moles) of hexamethylene dibromide was added over a period of 1¼ hours, the temperature of the reaction mixture being maintained at 112–115° C. throughout this period. The reaction mixture was then heated at 115° C. for two hours, cooled and the salt formed was dissolved in water made alkaline with sodium carbonate. The organic solvent phase was separated from the aqueous phase and the solvent flashed off at 100° C. on the vacuum pump. The crude product weighed 922 grams. This product was stabilized with NaOH in methyl alcohol, and washed thoroughly. It was distilled on a falling-film type molecular still at 125° C. at 0.1 millimeter mercury pressure. There was obtained 241 grams of a water-white liquid product, which represented a yield of bis-1,6-(dibutyl phosphono)hexane of 51.2% based on the hexamethylene dibromide charged. The product had the following characteristics: specific gravity (20/4)=1.1025; refractive index (20/*d*)=1.4519; weight percent phosphorus—found=13.2%; calculated=13.2%; weight percent carbon—found=55.8%; calculated=56.1%; weight percent hydrogen—found=10.4%; calculated=10.2%.

One property of the diphosphorus esters of this invention which distinguishes them from the more commonly employed mono phosphates, such as trioctyl phosphate, is their exceptional behavior with respect to corrosion. These materials have been found to be substantially non-corrosive with respect to copper, magnesium, iron, cadmium, or aluminum. As a class, the new diphosphorus esters have suitable properties for use as hydraulic fluids. In general, their viscosities are between 10 and 25 centistokes at about room temperature.

The new diphosphorous esters have flash and fire points of outstanding superiority. They are highly resistant to oxidation, especially as shown by the low percentage of increase in viscosity caused by extended heating in the presence of oxygen.

The phosphorus compounds of this invention may be used without further modification as hydraulic fluids. However, in some cases, the viscosity characteristics of the diphosphorus esters may be improved by the addition thereto of polymerized esters of the acrylic acid series (poly alkyl acrylates), such as acrylic acid esters, and more preferably, methacrylic acid esters. The latter are readily available as commercial products and are sold under the trade name "Acryloid." The esters to be used should have molecular weights from about 5,000 to about 25,000, preferably 5,000 to 15,000. It will be understood that this is an average figure for the mixture of polymers which is always present.

The acrylic acids should be esterified with aliphatic alcohols having 2 to 15 carbon atoms (preferably 4 to 12 carbon atoms) and the polymers may be polymers of a single ester or may be copolymers of a mixture of such esters. The term "polymerized ester" or "poly alkyl acrylates" will be understood to include both of these types.

The polymeric esters are generally available as concentrated dispersions in a solvent such as kerosene and commercially available varieties usually contain about about equal amounts of the polymer and solvent. The polymer should be employed in an amount at least sufficient materially to thicken the composition and still more preferably also to improve the viscosity index of the composition. Ordinarily, the amount necessary for this effect will vary between about 0.5 and 5% by weight of the total composition dependent upon the original viscosity index thereof and the desired improved effect contemplated.

While the diphosphorus esters of this invention them-

selves may be used as hydraulic fluids, they may also be employed in the improvement of other hydraulic fluids or lubricating compositions. In the latter instance the compositions may also contain from 5 to 50% by weight based on the weight of the esters, of a diluent or solvent, such as glycols, other phosphorus esters, alkene oxide polymers, esters of dicarboxylic acids, hydrocarbons and the like. Typical members of these groups include the monobutyl ether of ethylene glycol, the monoethyl ether of triethylene glycol, the methyl ethyl ether of diethylene glycol, poly oxypropylene glycol, tricresyl phosphate, trioctyl phosphate, di-2-ethylhexyl sebacate and light lubricating oils, kerosene, and the like.

The improvement in corrosion characteristics and oxidation stability is raised to a high level by the addition of epoxide compounds, particularly epoxy ethers, and/or sulfur containing organic compounds, in an amount between about 0.05 and 5% by weight of the total composition. Glycidyl ethers have been found to be especially effective, such as glycidyl phenyl ether, glycidyl benzyl ether, glycidyl isopropyl ether, and glycidyl orthocresyl ether. Other epoxides suitable for this purpose include isobutylene oxide, pentadiene monoxide, styrene oxide, 2,3-epoxypentane and epichlorohydrin. Typical sulfur-containing organic compounds especially suitable are the hydrocarbyl sulfides and particularly the hydrocarbyl disulfides, including dialkyl sulfides or aryl disulfides, such as benzyl disulfide, butyl disulfide and wax disulfide.

Other ingredients which may be employed, together with those already described, includle gelling agents, suitable for the preparation of thickened lubricants having thixotropic properties or greases. The gelling agents found to be especially suitable are either high molecular weight soaps of fatty acids or hydroxy fatty acids such as sodium stearate, lithium hydroxystearate, calcium oleate, or aluminum palmitate, or inorganic colloidal materials including silica, magnesia, alumina, and oleophilic clay-like materials. These colloids should be in the gel form, having an expanded structure resembling an aerogel. Preferably, they are present in amounts between 1 and 10% by weight of the total composition if a grease structure is desired.

EXAMPLE III

Table I shows data relating to the suitability of the present class of compounds for use as non-flammable hydraulic fluids.

Details of some of the tests reported in the foregoing table are given below:

Thermal stability test.—The thermal stability test comprises heating approximately 20 cubic centimeters of sample in a closed tube under CO_2 atmosphere for 24 hours at 150° C., followed by determination of viscosity and viscosity index change.

Semi-micro flash point.—A cup modeled on the Cleveland open cup apparatus was used, but scaled down to hold a 10 cubic centimeter sample instead of the usual 70 cubic centimeter employed in the ASTM Open Flash test.

Pipe cleaner flammability test.—A pipe cleaner, reduced to 4¼ inches in length, is saturated with fluid to be tested, the excess drained off and the cleaner inserted in a metal holder. It is then cycled at 36 revolutions per minute between two electric hot plates mounted horizontally ½ inch apart with a grid of ceramic spaghetti over the open coil heaters. The temperature between the two grids varies between 710 and 760° C., dropping during the test. The number of cycles made before the fire occurred is given in the foregoing table.

Oxidation-corrosion test.—Washers of various metals were placed on a glass standard fixed in a tube containing the liquid to be tested. Air was bubbled at a standard rate through the same for 71 hours at 121° C. The weight loss of the washers was determined in order to estimate the corroding effect of the test liquid on the specific metal.

The data set out in Table I demonstrates the marked difference (over 125° F.) between the pour point (+60° F.) of neutral alkyl esters of ethane diphosphoric acid having less than nineteen carbon atoms and the pour points (below −65° F.) of the neutral C_3—C_9 alkyl esters of C_3—C_{10} alkane-diphosphoric acids of this invention.

The hydraulic fluids of the present invention may be used as fluid power and transmission media in any of the common hydraulic systems wherein power is transmitted from an actuable element to an actuated element by means of a fluid. The most common form of such a system comprises a pair of variable volume chambers with connecting conduit means, the chambers and conduit means being filled with a fluid hydraulic power transmission medium. The hydraulic fluids of the present invention may, of course, also be used in analogous equipment in which power transmission is not the primary purpose of design as, for example, in power absorption

Table I

Compound and Formula	Boiling Range, ° C.	Viscosity, cs., ° F.			Dean and Davis Vis. Ind.	Pour Pt., ° F.	Semi-Micro Flash Pt., ° F.	Pipe Cleaner Cycles, Fire	Oxidation Corrosion mg./cm.²	
		−40	100	210					Cu	Steel
Bis-1,2-(di-n-butyl phosphono)ethane $[(C_4H_9O)_2\overset{O}{\overset{\|}{P}}—CH_2]_2$	183 at 0.6 mm					+60			1.24	1.16 Mg +0.24 Fe 9.4 Cd +0.08 Al
Bis-1,3-(di-n-butyl phosphono)propane $[(C_4H_9O)_2\overset{O}{\overset{\|}{P}}—CH_2]_2CH_2$	199–205 at 5 mm		14.18	3.16	91	<−65		28		
Bis-1,4-(di-n-butyl phosphono)butane $[(C_4H_9O)_2\overset{O}{\overset{\|}{P}}—CH_2CH_2]_2$	132 at 1×10^{-5} mm	2,004	13.27	2.97	77.5	<−65	450	26		
Bis-1,6-(di-n-butyl phosphono)hexane $[(C_4H_9O)_2\overset{O}{\overset{\|}{P}}—CH_2CH_2CH_2]_2$	125 at 0.1 mm	3,550	19.86	4.17	131	<−65	480	24	1.16	0.44 Mg 0.04 Fe 0 Cd 0.04 Al

systems, such as damping mechanisms, shock absorbers, and the like.

This application is a continuation-in-part of my copending application Serial No. 382,482, filed September 25, 1953, which in turn is a continuation-in-part of copending application Serial No. 201,474, filed December 18, 1950, and now abandoned.

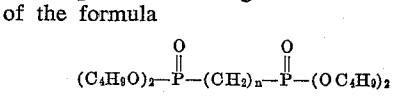
I claim as my invention:

1. As a new product bis-1,3-(dibutylphosphono)-propane.

2. As a new product bis-1,6-(dibutylphosphono)-hexane.

3. As a new product bis-1,6-((2-ethylhexyl)phosphono)hexane.

4. A compound containing at least 19 carbon atoms and of the formula



in which n is an integer from 3 to 6.

References Cited in the file of this patent

UNITED STATES PATENTS

2,634,288 Boyer et al. ---------- Apr. 7, 1953