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ORGANOPHOSPHONATES

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ABSTRACT OF THE DISCLOSURE

Organophosphonate compounds are provided represented by the structural formula:

$$R_1-\overset{O}{\overset{\|}{P}}-(OR)_2$$

wherein R_1 is a member selected from the group consisting of haloalkyl, alkenyl and haloalkenyl and R is a member selected from the group consisting of alkynyl, haloalkyl and haloalkenyl, with the proviso that when R and R_1 are haloalkyl, they are different.

This invention relates to organophosphonate compounds. More particularly, this invention relates to phosphonate esters of aliphatic phosphonic acids and aliphatic alcohols.

Organophosphonates have been found useful as corrosion inhibitors. The halogenated derivatives, i.e., generally, those containing at least 2 halogen radicals, have also been found useful as flame retardants. Fabrics containing such flame retardants for example, have been found to only char in the presence of an open flame and to immediately extinguish combustion in the absence of an open flame, thereby eliminating the presence of a potentially dangerous afterglow upon removal of the flame.

Accordingly, it is an object of the present invention to provide new organophosphonate compounds.

It is another object of the present invention to provide flame retardants for fibrous materials.

It is still another object of the present invention to provide organophosphonate compounds useful as corrosion inhibitors.

These as well as other objects are accomplished by the present invention which provides organophosphonate compounds represented by the structural formula:

$$R_1-\overset{O}{\overset{\|}{P}}-(OR)_2$$

wherein R_1 is a member selected from the group consisting of haloalkyl, alkenyl and haloalkenyl and R is a member selected from the group consisting of alkynyl, haloalkyl, and haloalkenyl, with the proviso that when R and R_1 are haloalkyl, they are different.

A preferred clas of organophosphonates are those represented by the structural formula:

$$X-\overset{O}{\overset{\|}{P}}-(OY)_2$$

wherein X is a member selected from the group consisting of haloethyl, haloxinyl and vinyl radicals and each Y is a member independently selected from the group consisting of propargyl, halopropyl and haloallyl radicals.

Illustrative compounds included within this class are, for example,

dipropargyl β-chloroethyl phosphonate,
dipropargyl vinyl phosphonate,
di(2,2,3,3-tetrabromopropyl)-1-bromovinyl phosphonate,
di(2,2,3,3-tetrabromopropyl) 1,1,2,-tribromoethyl phosphonate,
2,2,3,3-tetrabromopropyl-2,3-dibromoallyl-β-chloroethyl phosphonate,
di(2,3-dichloroallyl) vinyl phosphonate,
dipropargyl 1,2-dichloroethyl phosphonate,
dipropargyl 1,2,2-tribromoethyl phosphonate
and the like.

The organophosphonates of the present invention are generally prepared by reaction of aliphatic phosphonic acids or acid chlorides with aliphatic alcohols. Preferably, a two carbon aliphatic phosphonic acid or acid chloride such as a haloethyl, halovinyl or vinyl phosphonic acid or acid chloride is employed. The two carbon aliphatic phosphonic acid or acid chloride is preferably reacted with a three carbon aliphatic alcohol such as propargyl alcohol, a halopropyl alcohol or a haloallyl alcohol.

It is considered preferable when employing phosphonic acid chlorides to remove the hydrochloric acid generated by charging hydrochloric acid scavengers to the reaction system. Any organic or inorganic base is suitable for use as a scavenger, for example pyridine, N-methyl piperidine, triethylamine, sodium hydroxide, potassium hydroxide and the like can be employed.

The reaction proceeds readily at room temperature, however, any temperature from about room temperature or below to about the reflux temperature of the reaction mixture can be suitably employed, if desired. To obtain the higher halogenated species, it had been found most convenient to form unsaturated phosphonic acid esters and to add the desired halogen in either gaseous or liquid form to a solution thereof. Although any halogen can be employed for purposes of the present invention, it is considered preferable to employ bromine or chlorine. If desired, the reaction can proceed in the presence of a suitable inert solvent. Generally halogenated hydrocarbons such as carbon tetrachloride, chloroform, ethylene dichloride, trichloroethylene, perchloroethylene and the like can be suitably employed. The organophosphonates of the present invention can be recovered from the reaction medium by conventional recovery techniques.

The halogenated organophosphonate compounds of the present invention can be applied to fibers and fabrics to impart flame retardance thereto in any suitable vehicle. Generally these compounds are soluble in halogenated hydrocarbons such as carbon tetrachloride, chloroform, methylene chloride, trichloroethylene, perchloroethylene and the like in other solvents such as tetrahydrofuran. Solutions or dispersions containing the flame retardant compositions of the present invention in concentrations ranging from about 5 to about 10 percent by weight can be suitably employed.

The flame retardant compositions can be applied to fibers and fabrics by any convenient means such as spraying, dipping, immersing, padding and the like. If desired, the flame retardant compositions can be admixed with synthetic polymeric materials and can be co-extruded therewith to form fibers exhibiting flame retardation. Generally, it is considered preferable to impart from about 5 to about 20 percent, by weight on a dry basis of the flame retardant compositions to the fibers and fabrics being treated to obtain effective flame retardation.

Both synthetic and natural fibers and the fabrics made therefrom can be treated in accordance with the present invention. Typical fibers which can be treated are, for ex-

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ample, cotton, wool, silk, nylon, rayon, polyesters and the like.

It has been found that when the halogenated organophosphonates of the present invention are applied to fibers and fabrics in the manner described hereinabove, the resulting materials will not support combustion and will only char in the presence of an open flame. Upon removal of the flame, burning immediately ceases without an afterglow.

The following examples further define, describe and compare methods of preparing the organophosphonates of the present invention and of employing these compounds to impart flame retardation to fibrous materials. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

Into a 250 milliliter three neck flask fitted with a mechanical stirrer, thermometer and dropping funnel was placed 36 grams (0.2 mole) of β-chloroethyl phosphonyl dichloride, 22.4 grams (0.4 mole) propargyl alcohol and 100 milliliters of sodium dried benzene. To the solution, was added dropwise 40 grams (0.4 mole) of triethylamine at such a rate that the temperature never exceeded 30° C. A solid was formed. The mixture was stirred for 1½ hours after the addition had been completed. The mixture was filtered and the solid washed with benzene and dried under vacuum. The solid was found to weigh 51.7 grams (94% yield) and was identified as triethylammonium chloride. The benzene extracts were combined and the solvent removed by distillation. The residue was fractionated through a one foot Vigreux column. In this manner 22.1 grams (50%) of dipropagyl β-chloroethyl phosphonate were isolated exhibiting a boiling point of 125° C. at 0.1 mm. Hg.

Analysis.—Calcd. for $C_8H_{10}ClO_3P$ (percent): C, 43.56; H, 4.57; Cl, 14.07; P, 16.08. Found (percent): C, 43.77; H, 4.72; Cl, 14.00; P, 16.47.

Infrared: C≡CH, 2120 cm.$^{-1}$; P≡O, 1250 cm.$^{-1}$; POC, 1024 cm.$^{-1}$; and 942 cm.$^{-1}$.

The structure was confirmed by nuclear magnetic resonance (NMR) which showed (relative to tetramethylsilane): C≡CH 2.9 p p.m. (triplet); ≡C—CH_2 4.5–4.9 p.p.m. (pair of doublets); ClH_2(3.5–4.0 p.p.m. (multiplet); CH_2P 2.1–2.7 p.p.m. (multiplet).

EXAMPLE 2

Employing the procedure of Example 1, 76 grams (0.42 mole) of β-chloroethyl phosphonyl dichloride was reacted with 47 grams (0.84 moles) of propargyl alcohol in 200 milliliters of benzene. Eighty-four grams (0.84 mole) of triethylamine was added dropwise to the reaction mixture at such a rate that the temperature never exceed 30° C. In this manner 106.6 grams (93% yield) of triethylamine hydrochloride was obtained. Also, 87.8 grams (93% yield) of undistilled dipropargyl β-chloroethyl phosphonate was obtained. Elemental analysis indicated that this compound was at least 92% pure.

EXAMPLE 3

To a stirred mixture of 110 grams (0.5 mole) of dipropargyl β-chloroethyl phosphonate prepared as described in Example 2, in 1000 milliliters of carbon tetrachloride, was added dropwise 320 grams (2.0 moles) of bromine while a temperature of 20° C. was maintained within the reaction medium. When the addition was completed, the reaction mixture was stirred for 24 hours at room temperature. The mixture was then washed with aqueous sodium bisulfite, water and dried over anhydrous sodium sulfate. When the solvent was removed from the filtered solution, there remained 400 grams of a viscous, light brown oil. This oil was identified as a mixture of di-(2,2,3,3 - tetrabromopropyl) β-chloroethyl phosphonate and 2,2,3,3-tetrabromopropyl-2,3-dibromoallyl, β-chloroethyl phosphonate.

Analysis.—Calcd. for $C_8H_{10}Br_8ClPo_3$ (percent): C, 11.18; H, 1.18; Cl, 4.13; Br, 73.38; P, 3.60.

Analysis.—Calcd. for $C_8H_{10}Br_6ClPO_3$ (percent): C, 13.88; H, 1.59; Cl, 5.07; Br, 67.16; P, 4.43. Found (percent): C, 13.44; H, 1.46; Cl, 6.71; 6.43; Br, 69.30, 68.58; P, 3.76, 3.82.

Nuclear magnetic reasonance analysis (relative to tetramethylsilane) indicated:

P.p.m.	Relative intensity	Assignment
6.25 singlet	1	CBr_2H
4.85 doublet	2	CH_2O
3.8 multiplet	1	CH_2Cl
2.6 multiplet	1	CH_2P

EXAMPLE 4

A solution of 44 grams (0.2 mole) of dipropargyl β-chloroethyl phosphonate and 22 grams (0.2 mole) of triethylamine in 100 milliliters of benzene was refluxed for one hour. A white solid was formed. When the solid was removed by filtration, there was obtained 20 grams (75% yield) of triethylammonium chloride. The solvent was evaporated from the filtrate leaving 37 grams (100%) of dipropargyl vinylphosphonate.

The structure was confirmed by nuclear magnetic reasonance analysis (relative to tetramethylsilane) which showed the following:

P.p.m.	Relative intensity	Assignment
5.8–6.8 (multiplet)	3	CH_2=CH
4.6–4.8 (pair of doublets)	4	OCH_2
2.8 (triplet)	2	C≡CH

EXAMPLE 5

To a solution of 16 grams (0.1 mole) of dipropargyl vinyl phosphonate in 50 milliliters of chloroform was dropwise 80 grams (0.5 mole) bromine. After the addition, the reaction mixture was stirred at room temperature for 24 hours and then refluxed for five hours. When the reaction mixture had cooled to room temperature, it was washed with aqueous sodium, bisulfite, water and dried over anhydrous sodium sulfate. Upon removal of the solvent, there remained 64 grams (96%) of a brown viscous liquid. The nuclear magnetic resonance spectrum showed the presence of a CBr_4H group and did not indicate the presence of vinyl or acetylenic hydrogens.

EXAMPLE 6

A solution of 66 grams (0.1 mole) of di(2,2,3,3-tetrabromopropyl) 1,2-dibromoethyl phosphonate and 10 grams (0.1 mole) of triethylamine in 100 milliliters of benzene was refluxed for one hour. The reaction mixture was filtered after being cooled to room temperature yielding 18 grams (100%) of triethylammonium bromide. When the solvent was removed, there remained 58 grams (100%) of di(2,2,3,3-tetrabromopropyl) 1-bromovinyl phosphonate.

EXAMPLE 7

To a solution of 58 grams (0.1 mole) of di(2,2,3,3-tetrabromopropyl) 1-bromovinyl phosphonate prepared in the manner described in Example 6, in 100 milliliters of chloroform was added 16 grams (0.1 mole) bromine. The reaction was stirred for one day at room temperature and then washed with aqueous sodium bisulfite, water and dried over anhydrous sodium sulfate. When the solvent was removed, there remained 64 grams (100%) of di(2,2,3,3-tetrabromopropyl) 1,1,2-tribromoethyl phosphonate.

EXAMPLE 8

A solution of 5 grams of di(2,2,3,3-tetrabromopropyl) 1-bromovinyl phosphonate prepared in the manner described in Example 6 in 45 grams of tetrahydrofuran to-

gether with 32.5 grams of Freon 11 and 17.5 grams of Freon 12 was charged to a suitable aerosol bottle. The solution was sprayed onto cotton broadcloth to a 17% dry weight pickup. The cloth when so treated charred when held in the flame of a burning match. The cloth stopped burning immediately upon removal of the flame. There was no afterglow.

Although specific materials and conditions were set forth in the above exemplary processes for making and using the organophosphonate compounds of the present invention, these are merely intended as illustrations of the present invention. Various other organophosphonates, vehicles and modes of application such as those listed above may be substituted in the examples with similar results.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

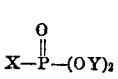
1. An organophosphonate represented by structural formula:



wherein R_1 is a member selected from the group consisting of halo-lower alkyl and halo lower alkenyl and R is a member selected from the group consisting of lower alkynyl, halo lower alkyl and halo lower alkenyl, with

the proviso that when R and R_1 are haloalkyl, they are different.

2. An organophosphonate represented by the structural formula:



wherein X is a member selected from the group consisting of haloethyl and halovinyl radicals and Y is a member independently selected from the group consisting of propargyl, halopropyl and haloallyl radicals.

3. An organophosphonate as defined in claim 2 which is dipropargyl β-chloroethyl phosphonate.

4. An organophosphonate as defined in claim 2 which is di(2,2,3,3-tetrabromopropyl) 1-bromovinyl phosphonate.

5. An organophosphonate as defined in claim 2 which is di(2,2,3,3-tetrabromopropyl) 1,1,2-tribromoethyl phosphonate.

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