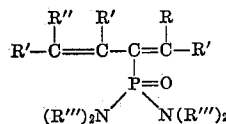
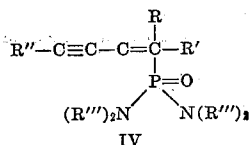
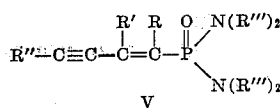
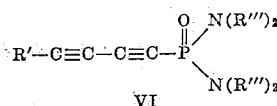


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PHOSPHONIC DIAMIDES

21 Claims. (Cl. 260—80)

$$\begin{array}{c} \text{O} \quad \text{N(R''')}_2 \\ \parallel \quad \diagup \\ \text{A-P} \\ \diagdown \\ \text{N(R''')}_2 \end{array}$$
$$\begin{array}{ccccccc} & \text{R}'' & \text{R}' & \text{R}' & \text{R} & \text{O} & \text{N(R''')}_2 \\ & | & | & | & | & || & / \\ \text{R}' - & \text{C} = & \text{C} - & \text{C} = & \text{C} - & \text{P} & \backslash \\ & & & & & & \text{N(R''')}_2 \end{array}$$
$$\begin{array}{c} \text{R}'' \quad \text{R}' \\ | \quad | \\ \text{R}' - \text{C} = \text{C} - \text{C} \equiv \text{C} - \text{P} \begin{array}{l} \nearrow \text{O} \text{N(R}'')_2 \\ \searrow \text{N(R}'')_2 \end{array} \\ \text{II} \end{array}$$


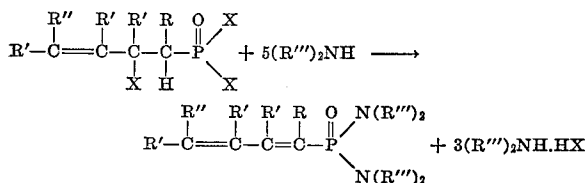
Further, according to the invention, there are provided new compositions of matter comprising polymers of the

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novel phosphonic diamides represented by the above structural formulas.

Still further according to the invention, there is provided a method of preparing the phosphonic diamides represented by the above structural formulas.

A preferred method of preparing these new unsaturated hydrocarbon phosphonic diamides is by reacting under anhydrous conditions a haloalkene-phosphonic dihalide containing at least one olefinic double bond with an amine containing at least one hydrogen attached to the nitrogen atom or with ammonia in an amount in excess of the stoichiometric quantity needed. When employing strongly basic amines the reaction is believed to proceed according to the following equation:



where R, R', R'', and R''' are groups as defined above, and X is either Cl or Br.

It is desirable to use at least 4 mols of amine to one mol of haloalkenephosphonic dihalide to bring about complete amidation, plus an additional mol of amine for each chlorine which is attached to carbon and which is to be removed by dehydrohalogenation. When a relatively weak amine is employed the dehydrohalogenation may not occur simultaneously with the amide formation. In such instances, if it is desired to dehydrohalogenate it will be necessary to treat the amide with a relatively strong base in a subsequent step.

One method of operation is to add the haloalkenephosphonic dihalide, with constant stirring, to an excess of the amine, either undiluted or diluted with a suitable solvent. The reaction is usually effected at a temperature in the range between 0 and -70°C ., preferably between -40 and -50°C . After the reaction is substantially complete, the excess amine is removed by suitable means, as, for example by gentle warming. Ether is then added to facilitate separation of the amine hydrohalide, which is then removed from the reaction mixture by filtration. After the ether has been removed by evaporation at room temperature, the unsaturated hydrocarbon phosphonic diamide is separated from the residual mixture by conventional means, such as, for example, by fractional distillation under reduced pressure. In some instances, a portion of the product polymerizes during purification and a polymer remains in the reactor. Amines which are applicable are primary and secondary amines of the formula

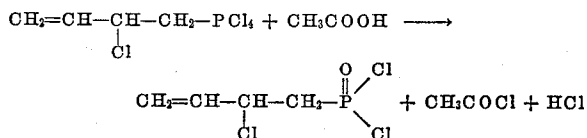


where R''' is the same as heretofore defined. Although in general primary and secondary amines are applicable I prefer to use the primary or secondary aromatic amines, such as aniline, N-methylaniline, 2-aminoquinoline, 2-naphthylamine, diphenylamine, o-tolylamine; and secondary aliphatic, carbocyclic, or heterocyclic amines, such as diallylamine, dicyclohexenylamine, di-2-butenylamine, dimethylamine, dicyclohexylamine, piperidine, and morpholine. Additional examples of amines are allylamine, alpha-allylbenzylamine, bis-(p-2-butenylphenyl)amine, dicinnamylamine, and 4-phenylbutylamine. In some instances ammonia can be used to produce the amide.

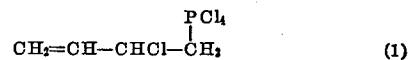
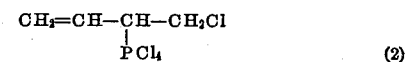
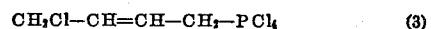
In my copending application, Serial No. 425,769, filed April 26, 1954, there are set forth, described and claimed certain haloalkenephosphonic dihalides and a method of preparation therefor. The haloalkenephosphonic dihalides of said application, which have a hydrogen atom attached to the same carbon atom to which the phosphorus atom is attached, are among those suitable as starting materials

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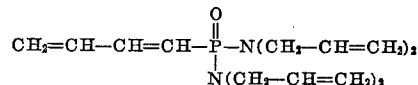
for the preparation of phosphonic diamides of this invention. As stated therein, the said dihalides are preferably prepared by reacting the corresponding haloalkenephosphorus tetrahalide with a carboxylic acid. Thus, 2-chloro-3-butenephosphorus tetrachloride, which is the preferred starting material, is reacted with acetic acid in accordance with the following equation:



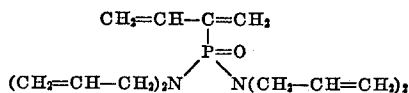
As stated in the above referred to application when 1,3-butadiene is reacted with phosphorus pentachloride to form a chlorobutenephosphorus tetrachloride three possible isomers can be obtained, i. e.,



At present it is believed that isomer No. 1, above, predominates. When a mixture of the said isomers is reacted with a carboxylic acid according to the above given equation a mixture of the corresponding chlorobutenephosphonic dichlorides is obtained. Thus, when a mixture of the said chlorobutenephosphonic dichlorides is used as a starting material in the reaction with an unsaturated amine such as diallylamine the corresponding alkadienephosphonic diamides are obtained, i. e.,

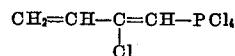


N,N,N',N'-tetraallyl-1,3-butadiene-1-phosphonic diamide and

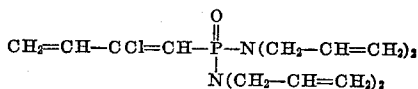


N,N,N',N' - tetraallyl - 1,3 - butadiene - 2 - phosphonic diamide.

When vinylacetylene is reacted with phosphorus pentachloride to form a chlorobutadienephosphorus tetrachloride one of the isomers which can be obtained has the following structure:



When this isomer is reacted with a carboxylic acid according to the above given equation the corresponding chlorobutadienephosphonic dichloride is obtained. Thus, when the said chlorobutadienephosphonic dichloride is used as a starting material in the reaction with an unsaturated amine such as diallylamine the corresponding chloroalkadienephosphonic diamide is obtained, i. e.



N,N,N',N' - tetraallyl - 2 - chloro - 1,3 - butadiene - 1-phosphonic diamide.

Where preferable, dehydrohalogenation involving a halogen atom attached to a carbon atom can be accomplished by a separate step additional to the amidation step, such as, for example, by treatment of a haloalkenephosphonic diamide with alcoholic potassium hydroxide, powdered potassium hydroxide, powdered sodium hydroxide, 2,6-dimethylpyridine or dimethylamine.

The products of this invention are valuable as plasticizers for a wide range of polymeric materials, including

synthetic resins and synthetic rubber. They are also useful as textile-treating agents, and as monomers in the formation of polymers and copolymers.

The polymers range from viscous liquids to brittle resins and rubbery solids.

Example I

The isomeric N,N,N',N' - tetraallyl - 1,3 - butadiene-phosphonic diamides were prepared by the following method:

To a solution of 107 g. (1.1 mol) of anhydrous diallylamine in 100 ml. of anhydrous ether, cooled to about -46°C ., was added dropwise, with constant stirring, 41.5 g. (0.2 mol) of the chlorobutenephosphonic dichloride, the preparation of which is described below (Example II). When all of the phosphonic dichloride had been added, the flask was warmed gently to room temperature, and the reaction was allowed to proceed with intermittent cooling to keep the temperature below 40°C ., until, after about one hour, cessation of heat evolution indicated that the reaction had proceeded substantially to completion. The precipitate of amine hydrochloride was removed by filtration, washed with ether, and dried. The ether was removed from the filtrate by distillation, and 100 ml. of n-pentane was added to precipitate the remaining amine hydrochloride, which was removed by filtration. The combined weights of the amine hydrochloride indicated a 98.5 percent yield of the theoretical total yield. Pentane and excess amine were stripped from the combined filtrates by distillation in vacuo, and the residue was distilled to yield the isomeric N,N,N',N'-tetraallyl-1,3-butadienephosphonic diamides, boiling at 157 to 170°C . at 1 mm. of Hg. Polymer formation occurred in the flask.

A sample prepared by a procedure similar to the one described above gave the following analysis:

Calculated for $\text{C}_{16}\text{H}_{25}\text{PON}_2$: C, 65.7; H, 8.6; P, 10.6. Found: C, 63.2; H, 8.9; P, 10.3.

Example II

The isomeric chlorobutenephosphonic dichlorides were prepared by the following procedure:

To a suspension of 454 g. of phosphorus pentachloride in 1200 cc. of dried benzene was added, with constant stirring, 250 g. of butadiene. After standing at 15 – 20°C . overnight, 100 cc. (about 60 g.) of butadiene were added to replace any butadiene that might have evaporated, and the suspension was stirred for 8 hours. The next day, an additional 100 cc. of butadiene was added, and the suspension was stirred for two hours. After cooling the flask in an ice bath, 2.2 mols of glacial acetic acid was added, while stripping off HCl, acetyl chloride, and some of the benzene in vacuo. The remainder of the solvent was then removed in vacuo from the resulting solution, and the residue distilled to yield 130 g. (33 percent) of chlorobutenephosphonic dichloride which boiled at 106°C . at 1.0 mm. Hg. It had the following characteristics: refractive index of 1.5185 at 25° under white light; density of 1.436 at room temperature, and molecular refractivity, calculated, 42.05; found, 43.85.

A sample prepared by the procedure similar to the one described above had a chlorine content of 50.4 percent, as compared with a calculated value of 51.2 percent.

Example III

A 500 ml. flask equipped with dropping funnel, stirring unit, and reflux condenser was placed in a Dry Ice-acetone bath. 107 g. (1.1 mol) of distilled diallylamine was agitated in the flask. Into this was dropped slowly 41.5 g. (0.20 mol) of chlorobutenephosphonic dichloride (prepared as described below in Example IV), dissolved in 100 ml. of ether. The reaction was exothermic with ready separation of the amine hydrochloride. 50 ml. more of ether was added and the mass filtered. The filtrate and 500 cc. of ether washings were combined. A faint cloud of precipitate settled slowly. The diallyl-

amine hydrochloride was dried for 3 hours at 105°C ., and then weighed. 72.9 g. were obtained, a 91 percent theoretical yield. The filtrate was stripped to 50°C ., under reduced pressure. 62.2 g. of a red, very viscous, jelly-

like oil remained. When it was attempted to distill 61.1 g. of this crude product at reduced pressure, 14.89 g. of diallylamine and 2.5 g. of a liquid boiling at 25°C ., at 0.45 mm. Hg. were obtained as overhead while polymerization occurred in the flask to yield 43.3 g. of a dark plastic solid.

Example IV

A second run was made for the purpose of preparing additional isomeric chlorobutenephosphonic dichlorides. 453 g. (2.17 mol) of PCl_5 was dissolved in 1500 cc. of vigorously refluxing benzene contained in a 3-liter, 3-necked flask which was equipped with a reflux condenser and dropping funnel. The flask was packed in ice, and cooled to below 40°C . 136 g. (2.52 mol) of butadiene dissolved in 300 cc. of benzene was then added over a 25 minute period. The material, packed in ice, was then stirred for 7 hours and allowed to stand overnight. To the pasty reaction mass was added dropwise, with constant stirring, 131 g. (2.18 mol) of acetic acid. The thick mixture turned clear, pale yellow. It was stripped with stirring to 25°C . at 20 mm. A dark tan oil, weighing 289.7 g. (64.4 percent theoretical) resulted. From 286.9 g. of this crude material was obtained 184.5 g. (41.5 percent theoretical) of a fraction boiling at 97 – 112°C . at 0.4 to 2.0 mm. Hg. It had a refractive index of n_D^{25} 1.5186.

Example V

The isomeric N,N,N',N'-tetramethyl-1,3-butadienephosphonic diamides were prepared by the following method:

To 100 g. of anhydrous dimethylamine, cooled in an acetone-Dry Ice bath, was added with stirring 41.5 g. of chlorobutenephosphonic dichloride, prepared as described above in Example II. The mixture was then allowed to warm to room temperature, and the excess dimethylamine was driven off by gentle heating. After adding 50 cc. of ether, the amine hydrochloride was removed by filtration, and washed with 100 cc. of ether. 46 g. of dimethylamine hydrochloride was obtained. The ether was removed from the filtrate, and the residue was distilled in vacuo to yield 21.5 g. of isomeric N,N,N',N'-tetramethyl-1,3-butadienephosphonic diamides, boiling at 102 – 120°C . at 1.25–2.5 mm. The residue remaining in the distillation flask was a clear, amber resin.

A sample prepared by a method similar to the one described above gave the following analysis:

Calculated for $\text{C}_8\text{H}_{17}\text{PON}_2$: C, 51.1; H, 9.11; P, 16.5. Found: C, 50.1; H, 9.6; P, 15.9.

Example VI

A second run was made for the purpose of preparing additional isomeric N,N,N',N'-tetramethyl-1,3-butadienephosphonic diamides. 100 g. (2.22 mol) of anhydrous dimethylamine was placed in a 500 cc. 3-necked flask, equipped with stirring unit, dropping funnel, and thermometer. It was cooled to -70°C . by means of a Dry Ice-acetone bath, and then into it was dropped slowly 42.5 g. (0.205 mol) of chlorobutenephosphonic dichloride which was prepared according to the procedure described above in Example IV. During this addition the temperature was maintained at -70° to -40°C . The amine hydrochloride separated readily. 50 cc. of ether was added. After two hours, the mixture was warmed gently. The precipitate of dimethylamine hydrochloride was filtered and washed well. 44.6 g. (88.8 percent theoretical) was obtained. The filtrate, which was a clear yellow oil, was stripped of ether, and then distilled under reduced pressure. 20.7 g. (53.7 percent theoretical) of a fraction boiling at 116 – 118°C . at 0.9 to 1.2 mm. Hg. was obtained. Its refractive index was n_D^{20} 1.5023.

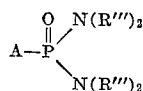
In the above examples anhydrous conditions were em-

ployed. While anhydrous conditions are preferred less than anhydrous conditions can be employed. Water reacts with the phosphonic dihalide causing it to hydrolyze, resulting in a lower yield. Otherwise, its presence is not harmful.

Although there is no reason to suspect that the structural formulas given as representing the compounds of the invention are incorrect, since said formulas were developed according to standard methods well known to those skilled in the art, the invention is not to be unduly limited by said formulas.

Obviously, one reading the above specification will realize that the various phosphonic diamides represented by the formulas given herein are not necessarily equivalents in the usual sense of that term but rather are alternatives each possessing different properties and, therefore, different uses.

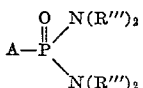
Reasonable variation and modification are possible within the scope of the foregoing disclosure and the appended claims to the invention, the essence of which is that: new compounds represented by the structural formula



defined hereinabove have been provided, said new compounds being phosphonic diamides characterized by either an alkapolyene grouping, an alkenyne grouping, an alkapolyene grouping or a five or six membered ring formed from one of said groupings, Formulas I, II, III, IV, V, and VI given herein being representative of said new compounds; new compositions of matter comprising polymers of said phosphonic diamides have been provided; and a method of preparing said phosphonic diamides which comprises reacting a halophosphonic dichloride with an amine.

I claim:

1. A phosphonic diamide represented by the structural formula



wherein: A is a member selected from the group consisting of unsubstituted and halogen-substituted alkapolyene, alkenyne and alkapolyene hydrocarbon radicals, and a five to six membered ring, said ring having a skeleton consisting of carbon atoms and having therein the carbon skeleton of one of said hydrocarbon radicals; R''' is a member containing from zero to ten carbon atoms selected from the group consisting of hydrogen, hydrocarbon, and heterocyclic radicals, said hydrocarbon radicals being selected from the group consisting of aromatic, saturated and unsaturated acyclic, and saturated and unsaturated alicyclic radicals, and combinations of the radicals as defined by R'''; and where, in addition, two R''' radicals together with the nitrogen atom attached thereto can form a heterocyclic ring containing from five to seven atoms, at least three of which are carbon, the remainder being selected from the group consisting of carbon, nitrogen, sulfur and oxygen.

2. N,N,N',N' - tetramethyl - 1,3 - butadiene - 1 - phosphonic diamide.

3. N,N,N',N' - tetramethyl - 1,3 - butadiene - 2 - phosphonic diamide.

4. N,N,N',N' - tetraallyl - 1,3 - butadiene - 1 - phosphonic diamide.

5. N,N,N',N' - tetraallyl - 1,3 - butadiene - 2 - phosphonic diamide.

6. A mixture of isomeric alkadienephosphonic diamides comprising N,N,N',N' - tetramethyl - 1,3 - butadiene - 1 - phosphonic diamide, and N,N,N',N' - tetramethyl - 1,3 - butadiene-2-phosphonic diamide.

7. A mixture of isomeric alkadienephosphonic diamides comprising N,N,N',N' - tetraallyl - 1,3 - butadiene - 1 - phosphonic diamide, and N,N,N',N' - tetraallyl - 1,3 - butadiene-2-phosphonic diamide.

8. Polymeric N,N,N',N' - tetramethyl - 1,3 - butadiene-1-phosphonic diamide.

9. Polymeric N,N,N',N' - tetramethyl - 1,3 - butadiene-2-phosphonic diamide.

10. Polymeric N,N,N',N' - tetraallyl - 1,3 - butadiene-1-phosphonic diamide.

11. Polymeric N,N,N',N' - tetraallyl - 1,3 - butadiene-2-phosphonic diamide.

12. A polymeric composition of matter comprising polymers of the isomeric mixture defined in claim 6.

13. A polymeric composition of matter comprising polymers of the isomeric mixture defined in claim 7.

14. The method of preparing a phosphonic diamide having a structural formula as defined in claim 1 which comprises reacting a haloalkenephosphonic dihalide with a compound selected from the group consisting of ammonia and an amine containing at least one hydrogen atom attached to the nitrogen atom.

15. The method of preparing a phosphonic diamide having a structural formula as defined in claim 1 which comprises reacting a haloalkenephosphonic dihalide with a compound selected from the group consisting of ammonia and an amine containing at least one hydrogen atom attached to the nitrogen atom to form a haloalkadienephosphonic diamide reaction product and reacting said product with a strong base.

16. The method of preparing a phosphonic diamide having a structural formula as defined in claim 1 which comprises: adding a haloalkenephosphonic dichloride to at least a stoichiometric quantity of a compound selected from the group consisting of ammonia and an amine containing at least one hydrogen atom attached to the nitrogen atom, dissolved in a suitable inert solvent to form a reaction mixture, maintaining said reaction mixture at a temperature within the range of 0 to -70° C. during said addition, warming said reaction mixture, maintaining said reaction mixture within the range of 0 to 100° C. until said reaction is substantially complete as indicated by cessation of heat evolution, filtering said reaction mixture to obtain a precipitate and a filtrate and recovering said phosphonic diamide from said filtrate.

17. The method of claim 16 wherein said amine is diallylamine, said halophosphonic dichloride is chlorobutenephosphonic dichloride and said alkapolyenephosphonic diamide is N,N,N',N' - tetraallyl - 1,3 - butadiene-phosphonic diamide.

18. The method of claim 16 wherein said amine is dimethylamine, said halophosphonic dichloride is chlorobutenephosphonic dichloride and said alkapolyenephosphonic diamide is N,N,N',N'-tetramethyl-1,3-butadienephosphonic diamide.

19. The product of the reaction between diallylamine and a chlorobutenephosphonic dichloride which has a boiling point ranging from 157 to 170° C. at 1 mm. of Hg.

20. The product of the reaction between dimethylamine and a chlorobutenephosphonic dichloride which has a boiling point ranging from 102 to 120° C., at 1.25 to 2.5 mm. Hg.

21. The product of the reaction between dimethylamine and a chlorobutenephosphonic dichloride which has a boiling point ranging from 116 to 118° C., at 0.9 to 1.2 mm. Hg.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,818,406

December 31, 1957

James N. Short

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

Column 2, line 33, for "and", second occurrence, read -- when --.

Signed and sealed this 27th day of January 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents