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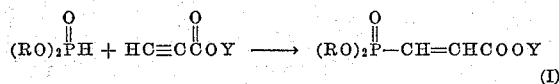
DIPHOSPHONATE ALKYL ESTERS

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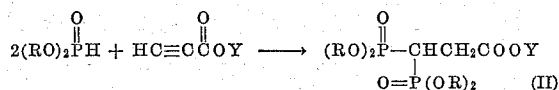
The present invention relates to organic compounds of phosphorus and more particularly provides a new method of preparing carboxylate phosphonates, some of which comprise a new and valuable class of organic phosphorus compounds.

According to the invention I prepare the carboxylate phosphonates by the addition reaction of a dialkyl phosphonate with an alkyl propiolate. The nature of the products which are formed depends upon whether one or two moles of the phosphonate add to the propiolate. By 1:1 addition, there are obtained dialkyl 2-carboalkoxyvinylphosphonates (I) substantially according to the scheme:



where R and Y are alkyl radicals of from 1 to 5 carbon atoms.

By 2:1 addition, there are obtained tetraalkyl 2-carboalkoxy-1,1-ethylidenediphosphonates (II) substantially according to the scheme:



in which R and Y are as above defined.

Reaction to give (II) appears to be favored, since even when there is used a 1:1 molar ratio of the dialkyl phosphonate and alkyl propiolate, a substantial quantity of the 2:1 addition product (II) is formed, plus the 1:1 addition product (I). Apparently, the 1:1 product, i.e., the dialkyl 2-carboalkoxyvinylphosphonate, containing as it does an olefinic double bond which is activated by the carboxylate radical, is so reactive that it competes with the alkyl propiolate for the available dialkyl phosphonate. The diphosphonate is thereby formed; and when the initial reaction mixture does not contain enough dialkyl phosphonate to provide for a theoretical yield of the diphosphonate, the reaction product will consist of the olefinic carboxylated monophosphonate, the saturated carboxylated diphosphonate, and unreacted alkyl propiolate. As the ratio of dialkyl phosphonate to alkyl propiolate exceeds 1:1, increasingly greater quantities of the diphosphonate will be formed. With a 2:1 dialkyl phosphonate to propiolate ratio, the product will be predominantly the diphosphonate. Thus, whether the reaction is conducted with a 1:1 or a 2:1 molar ratio of dialkyl phosphonate to alkyl propiolate, will be determined by whether or not it is desired to obtain a substantial yield of the olefinic carboxylate phosphonate (I). The quantity of (I) which is obtained will also be determined to some extent by the reaction conditions. Thus, a short reaction time is conducive to (I), since opportunity for subsequent conversion to (II) is thereby lessened.

Accordingly, depending upon the reaction conditions, the invention provides a method of obtaining a mixture of carboxylated phosphonates which consists essentially of either the dialkyl 2-carboalkoxyvinylphosphonates (I) or of the tetraalkyl 2-carboalkoxy-1,1-ethylidenediphosphonates (II). The compounds (I) can be readily separated from the compounds (II) by isolating procedures known to those skilled in the art, e.g., by fractional distillation, solvent extraction, etc.

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Dialkyl phosphonates suitable for reaction with alkyl propiolates to give the carboxylated phosphonates are simple or mixed dialkyl phosphonates having from 1 to 5 carbon atoms in the alkyl radical, e.g., dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, di-tert-butyl, dipentyl, diisopentyl, ethyl methyl, butyl propyl or methyl pentyl phosphonate. Examples of the useful propiolates are methyl, ethyl, propyl, isopropyl, isobutyl, butyl or pentyl propiolate.

Reaction of the dialkyl phosphonate with the alkyl propiolate proceeds readily at ordinary, decreased or increased temperatures and in the presence or absence of a basic or acidic catalyst and in the presence of an inert liquid diluent or solvent. Preferably, an organic basic catalyst is employed. This is particularly desirable when the reaction is effected in the presence of a diluent. Examples of presently useful basic catalysts are, e.g., the heterocyclic nitrogen bases such as N-methylmorpholine, pyridine, quinoline, N-ethylpiperidine, picoline, quinaldine, 4-methylpyrimidine, or N-phenylpyrazole; the tertiary amines such as triethylamine, triamylamine, tri-tert-butylamine, N,N-dimethylaniline and N-benzyl-N-methylaniline; alkylene polyamines such as triethylenediamine; quaternary ammonium compounds such as benzyltrimethylammonium methoxide or tetrabutylammonium butoxide; alkali metal alkoxides such as sodium or potassium methoxide or propoxide, etc. The quantity of catalyst to be used will depend upon the nature of the propiolate and of the dialkyl phosphonate; obviously the more reactive methyl or ethyl esters will require less catalyst than will the somewhat more sluggish higher alkyl esters. Whether or not a diluent is used will likewise regulate catalyst quantity. Also variable is the temperature at which reaction is effected; for, here again must be taken into consideration the nature of the reactants, catalyst quantity, and whether or not a diluent is used. The reaction is generally exothermic; hence, the present addition reactions can be conducted at ordinary room temperature or even at decreased temperatures, but heating of the reaction mixture may be needed to complete the reaction. All of these variables, i.e., catalyst quantity, use of diluent and temperature conditions can readily be arrived at by easy experimentation. Very rapid reaction at room temperature, as evidenced by rapid temperature rise, will show the need for a diluent and/or lower temperature and/or less catalyst. Conversely, no reaction or only a very slow reaction at room temperature will indicate the use of more extreme conditions, i.e., extraneous heating and/or no diluent and/or more catalyst. Thus, arrival at optimum reaction conditions is simply a matter of routine procedure by one skilled in the art.

The reaction product generally consists of the monophosphonate, i.e., the dialkyl 2-carboalkoxyvinylphosphonate, and of the diphosphonate, i.e., the tetraalkyl 2-carboalkoxy-1,1-ethylidenediphosphonate in varying proportions. If a diluent had been employed, it and any unreacted, excess dialkyl phosphonate and/or alkyl propiolate are removed by distillation, to leave as residue the mixture of said carboxylated monophosphonate and carboxylated diphosphonate. There is sufficient disparity, generally, in the boiling points of the two to permit separation thereof by easy fractional distillation. For some purposes separation will not be necessary.

To recapitulate: In the preparation of the carboxylated phosphonates by the presently provided process, the dialkyl phosphonate is mixed with the alkyl propiolate, preferably in the presence of a basic catalyst and in the presence or absence of an inert diluent or solvent at a temperature which may range from below room temperature to refluxing, say, at from 0° C. to 125° C., and the resulting mixture is allowed to stand until formation of

carboxylate—phosphonate product has occurred. The dialkyl phosphonate and the propiolate are employed in substantially equimolar proportions to obtain a mixture of the olefinic carboxylated monophosphonate and the saturated carboxylated diphosphonate; however, an excess of the dialkyl phosphonate may be used to obtain a preponderant quantity of the diphosphonate, or an excess of the propiolate may be used to increase the yield of the olefinic carboxylated monophosphonate. An excess of the propiolate may also serve as diluent. Extraneous, inert liquid diluents which are presently useful are, e.g., benzene, toluene, xylene, hexane, dioxane, nitrobenzene, acetone, hexachloroethane, etc.

Examples of carboxylated phosphonates which are prepared according to the invention from the indicated dialkyl phosphonate and the indicated alkyl propiolate are shown below:

Dimethyl 2 - carbomethoxyvinylphosphonate and/or tetramethyl 2 - carbomethoxy-1,1-ethylidenediphosphonate from methyl propiolate and dimethyl phosphonate.

Diethyl 2-carboethoxyvinylphosphonate and/or tetraethyl 2-carboethoxy-1,1-ethylidenediphosphonate from ethyl propiolate and diethyl phosphonate.

Dimethyl 2-carboethoxyvinylphosphonate and/or tetramethyl 2 - carboethoxy-1,1-ethylidenediphosphonate from ethyl propiolate and dimethyl phosphonate.

Dibutyl 2-carbomethoxyvinylphosphonate and/or tetra-butyl 2 - carbomethoxy-1,1-ethylidenediphosphonate from dibutyl phosphonate and methyl propiolate.

Dipentyl 2-carbopropoxyvinylphosphonate and/or tetra-pentyl 2-carbopropoxy-1,1-ethylidenediphosphonate from dipentyl phosphonate and propyl propiolate.

Diisopropyl 2 - carbomethoxyvinylphosphonate and/or tetraisopropyl 2 - carbomethoxy-1,1-ethylidenediphosphonate from diisopropyl phosphonate and methyl propiolate.

Ethyl methyl 2-carbobutoxyvinylphosphonate and/or diethyl dimethyl 2-carbobutoxy-1,1-ethylidenediphosphonate from ethyl methyl phosphonate and butyl propiolate.

Dipropyl 2 - carbopentyloxyvinylphosphonate and/or tetrapropyl 2-carbopentyloxy-1,1-ethylidenediphosphonate from dipropyl phosphonate and pentyl propiolate.

The dialkyl 2-carboalkoxyvinylphosphonates which are prepared by the presently provided process are compounds which are useful for the preparation of synthetic resins and plastics either by homopolymerization or by copolymerization with copolymerizable monomers, e.g., styrene, vinyl acetate, acrylonitrile, methyl methacrylate, ethyl acrylate, vinylpyrrolidone, etc. They are likewise useful as intermediates, e.g., for the preparation of dialkyl 2-carboalkoxy-1,2-dichloroethylphosphonates by reaction with chlorine.

The presently provided tetraalkyl 2-carboalkoxy-1,1-ethylidenediphosphonates are new, well defined compounds which range from viscous oils to waxy or crystalline solids. They are advantageously used for a variety of industrial and agricultural purposes, e.g., as plasticizers for synthetic resins, as gasoline and lubricant additives, and as plant-growth regulators. When employed as a foliage spray on either broad-leaf or narrow-leaf plants, at an 0.5% concentration, they have a growth-retarding effect thereon, but do not kill the plants. Premature cropping and unwanted exuberance of foliage is thereby prevented. When employed as additives to leaded gasoline, the presently provided diphosphonates serve to inhibit spark-plug fouling.

The invention is further illustrated by, but not limited to, the following examples:

Example 1

A mixture consisting of 8.4 g. (0.1 mole) of methyl propiolate and 50 ml. of benzene was added dropwise to a mixture consisting of 13.8 g. (0.1 mole) of diethyl phosphonate, 50 ml. of benzene and 1 ml. of 40% methanolic trimethylbenzylammonium hydroxide. The temperature of the reaction mixture rose exothermally to about 50° C. The red-orange reaction mixture was then heated at reflux for 6 hours to assure complete reaction. After being allowed to cool to room temperature it was washed first with 50 ml. of saturated, aqueous ammonium chloride and 50 ml. of distilled water. The solvent was removed from the washed product by distillation and the residue was fractionated via a Vigreux column to give (I), 0.9 g., B.P. 98–99° C., comprising diethyl 2-carbomethoxyvinylphosphonate and (II), 5.2 g., B.P. 100–156° C. (chiefly 149–156° C.)/0.4–0.5 mm. n_D^{25} 1.4444, comprising tetraethyl 2-carbomethoxy-1,1-ethylidenediphosphonate.

Example 2

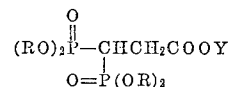
A mixture consisting of 8.4 g. (0.1 mole) of methyl propiolate and 50 ml. of benzene was added cautiously to a mixture consisting of 13.8 g. (0.1 mole) of diethyl phosphonate, 50 ml. of benzene and 0.5 ml. of 40% aqueous methanolic trimethylbenzylammonium hydroxide. A mild exothermic reaction occurred, and the reaction mixture darkened. After heating at reflux for 12 hours, the solvent was removed by distillation and the residue was fractionated via a Vigreux column to give (A), a fraction, B.P. 99–102° C./0.4 mm., comprising diethyl 2-carbomethoxyvinylphosphonate, and (B) a fraction, B.P. 130–156° C. (mostly 153–156° C.)/0.4 mm., n_D^{25} 1.4450, comprising tetraethyl 2-carbomethoxy-1,1-ethylidenediphosphonate.

Fraction B was combined with Fraction II of Example 1, and redistilled to give the substantially pure tetraethyl 2-carbomethoxy-1,1-ethylidenediphosphonate, B.P. 166–167° C./0.5 mm., n_D^{25} 1.4462, which analyzed as follows:

	Found	Calc'd for $C_{12}H_{26}O_8P_2$
Percent C.....	40.01	40.00
Percent H.....	7.25	7.27
Percent P.....	17.06	17.20

What I claim is:

1. Tetraethyl 2 - carbomethoxy - 1,1 - ethylidenediphosphonate.
2. A diphosphonate of the formula



where R and Y are alkyl radicals of from 1 to 5 carbon atoms.

References Cited in the file of this patent

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