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PROCESS FOR THE PRODUCTION OF MIXED PHOSPHONIC ACID ESTERS

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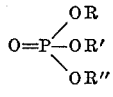
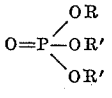
U.S. Cl. 260—982 1 Claim

ABSTRACT OF THE DISCLOSURE

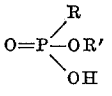
A process for the production of phosphonic acid esters of the formula



wherein R stands for a hydrocarbon radical containing 1–18 carbon atoms, R′ stands for an alkyl radical containing 1–3 carbon atoms and R″ for an alkyl or aralkyl radical containing 4–18 carbon atoms or for an alkenyl radical containing 3–18 carbon atoms comprising reacting phosphonic acid diesters of the formula

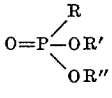


wherein R and R′ have the above meaning while heating with a halide of the formula R″X wherein R″ has the above meaning and X stands for chlorine, bromine or iodine in the presence of alkali metal, alkaline earth metal or ammonium salts of hydrohalic acids or partially esterified phosphonic acids of the formula



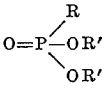
wherein R and R′ have the above meaning.

The present invention relates to mixed phosphonic acid esters and to a process for producing the same; more particularly it concerns a process for the production of mixed phosphonic acid esters of the general formula



I

in which R denotes a hydrocarbon radical containing 1–18 carbon atoms, while R′ stands for an alkyl radical containing 1–3 carbon atoms and R″ for an alkyl or aralkyl radical containing 4–18 carbon atoms or for an alkenyl radical containing 3–18 carbon atoms, wherein phosphonic acid diesters of the general formula

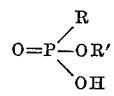


II

in which R and R′ have the above meaning, are reacted while heating with approximately equimolar amounts of

a halide of the formula R″X in which R″ has the above meaning and X stands for chlorine, bromine or iodine.

According to the present invention this process is carried out in the presence of alkali metal, alkaline earth metal or ammonium salts of hydrohalic acids or partially esterified phosphonic acids of the general formula



III

in which R and R′ have the above meaning.

Phosphonic acid diesters of the Formula II, which are suitable for the process of the invention are, for example, the dimethyl, diethyl or dipropyl esters of methane-, ethane-, propane-, butane-, hexane-, heptane-, octane-, nonane-, decane-, dodecane-, benzene-, benzyl-, methylbenzyl-, dimethylbenzyl-, indene-(2)-, ethylene-, propylene-, butylene- or 2-phenyl-ethylene-phosphonic acid.

Halides of the formula R″X are, for example, butyl pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, allyl, crotyl, nonenyl, decenyl, dodecenyl bromide or iodide as well as benzyl, methylbenzyl or dimethylbenzyl chloride, bromide or iodide.

The alkali metal or alkaline earth metal salts of hydrohalic acids or partially esterified phosphonic acids of the Formula III, which are to be used in the process of the invention, include, for example, the sodium, potassium, barium and calcium salts of hydrofluoric, hydrochloric, hydrobromic or hydroiodic acid or of the monomethyl, monoethyl and monopropyl esters of methane-, ethane-, propane-, butane-, hexane-, heptane-, octane-, nonane-, decane-, dodecane-, benzene-, benzyl-, methylbenzyl-, dimethylbenzyl-, indene-(2)-, ethylene-, propylene-, butylene- or 2-phenyl-ethylene-phosphonic acid. As ammonium salts there may be mentioned the salts of these hydrohalic acids or partially esterified phosphonic acids with ammonia, pyridine or an amine, such as diethylamine and triethylamine; the corresponding tetraalkyl ammonium salts, such as tetraethyl ammonium bromide or the tetraethyl ammonium salts of the monomethyl, monoethyl and monopropyl esters of the mentioned phosphonic acids are also suitable.

The amounts to be applied of these salts may vary within wide limits; in general, amounts of 1–5 mol of salt per 100 mol phosphonic acid diester according to Formula II will prove sufficient.

The reaction is expediently carried out at temperatures between 80 and 150° C. while stirring; it can be performed discontinuously or continuously. In the continuous process, the reaction mixture is passed through several stirring vessels connected in succession, while heating. The components are continuously introduced into the first stirring vessel and the reaction mixture is continuously withdrawn from the last stirring vessel and then worked up by conventional methods.

The mixed phosphonic acid esters which can be obtained according to the invention are suitable for a variety of applications; they can be used, for example, as plasticisers for synthetic resins, as flameproofing agents, as additives to motor fuels, as hydraulic oils and as extraction agents.

It is already known to produce mixed methane-, ethane- or propane-phosphonic acid diesters, one ester component of which contains 4–18 carbon atoms, by reacting the corresponding phosphonic acid dimethyl, diethyl or dipropyl esters with alkyl bromides or iodides containing 4–18 carbon atoms, while heating the reaction mixture to 160–230° C. Compared with this method wherein no

catalysts are applied to the process according to the invention is superior in that it can be carried out at a greater speed and at lower temperatures when the same reaction partners are used. In addition, the secondary reactions which occur in the known process to a considerable extent, such as e.g. the splitting off of hydrogen halide from the alkyl halide or the exchange of both ester groups of the diester employed are substantially repressed in the process according to the invention.

The following examples serve to illustrate the process according to the invention without, however, limiting its scope.

EXAMPLE 1

124 grams (1 mol) methane-phosphonic acid dimethyl ester and 137 g. (1 mol) butyl bromide are heated at 110° C. for 7 hours, while stirring, in the presence of 6.6 g. (0.05 mol) of the sodium salt of the monomethyl ester of methane-phosphonic acid, which was prepared by heating methane-phosphonic acid dimethyl ester with sodium fluoride, sodium chloride, sodium bromide or sodium iodide in a molar ratio of 1:1 at 100–140° C. The reaction mixture is then subjected to a vacuum distillation. 47 grams (0.28 mol) methane-phosphonic acid-O-methyl-O-butyl ester of B.P. 96–99° C./12 mm. Hg and refractive index n_D^{20} 1.4212 are obtained, besides 88 g. unreacted methane-phosphonic acid dimethyl ester. The yield amounts to 96.2%, referred to the reacted methane-phosphonic acid dimethyl ester.

EXAMPLE 2

124 grams (1 mol) methane-phosphonic acid dimethyl ester and 184 g. (1 mol) butyl iodide are heated at 120° C. for 7 to 10 hours, while stirring, in the presence of 6 g. sodium bromide, 3 g. ammonium chloride, 6 g. pyridine hydrochloride, 8 g. tetraethyl ammonium bromide, 4 g. diethylamine hydrochloride, 5 g. calcium chloride, 5 g. barium bromide or 5–10 g. of the alkali metal, alkaline earth metal or ammonium salts which can be obtained from methane-phosphonic acid dimethyl ester and the above salts by heating to 100–140° C.; the reaction mixture is subsequently subjected to a vacuum distillation. There are obtained 33 to 50 g. methane-phosphonic acid-O-methyl-O-butyl ester.

EXAMPLE 3

124 grams (1 mol) methane-phosphonic acid dimethyl ester and 152 g. (1 mol) isoamyl bromide are heated in the presence of 3 g. sodium bromide to 120° C., while stirring. After working up in the usual manner there are obtained 78 g. (0.44 mol) methane-phosphonic acid-O-methyl-O-isoamyl ester of B.P. 103–103.5° C./11 mm. Hg.

EXAMPLE 4

124 grams (1 mol) methane-phosphonic acid dimethyl ester and 249 g. (1 mol) dodecyl bromide are heated at 160° C. for 5 hours, while stirring, in the presence of 6 g. of the sodium salt of the monomethyl ester of methane-phosphonic acid, which was prepared by heating methane-phosphonic acid dimethyl ester with sodium fluoride, sodium chloride, sodium bromide or sodium iodide in a molar ratio of 1:1 at 100–140° C. After working up in the usual manner, there are obtained 83 g. (0.33 mol) methane-phosphonic acid-O-methyl-O-dodecyl ester of B.P. 153–157° C./1.5 mm. Hg and refractive index n_D^{20} 1.4410.

EXAMPLE 5

124 grams (1 mol) methane-phosphonic acid dimethyl ester and 122 g. (1 mol) allyl bromide are heated under reflux in the presence of 4 g. sodium bromide for 10 hours while stirring. After working up in the usual manner, there are obtained 82 g. (0.54 mol) methane-phosphonic acid-O-methyl-O-allyl ester of B.P. 88–90° C./13 mm. Hg.

EXAMPLE 6

124 grams (1 mol) methane-phosphonic acid dimethyl ester and 135 g. (1 mol) crotyl bromide are heated in the presence of 4 g. sodium bromide at 110° C. for 11 hours while stirring. After working up in the usual manner, there are obtained 62 g. (0.38 mol) methane-phosphonic acid-O-methyl-O-crotyl ester of refractive index n_D^{20} 1.4402.

EXAMPLE 7

124 grams (1 mol) methane-phosphonic acid dimethyl ester and 126.6 g. benzyl chloride are heated in the presence of 3 g. sodium chloride at 130° C. for 15 hours while stirring. After working up in the usual manner, there are obtained 60 g. (0.34 mol) methane-phosphonic acid-O-methyl-O-benzyl ester of B.P. 215–217° C./13 mm. Hg.

EXAMPLE 8

166 grams (1 mol) ethane-phosphonic acid diethyl ester and 137 g. (1 mol) butyl bromide are heated in the presence of 4 g. sodium bromide at 120° C. for 12 hours while stirring. After working up in the usual manner, there are obtained 40 g. (0.2 mol) ethane-phosphonic acid-O-ethyl-O-butyl ester of B.P. 111–113° C./13 mm. Hg and refractive index n_D^{20} 1.4175.

EXAMPLE 9

194 grams (1 mol) ethane-phosphonic acid diisopropyl ester and 249 g. (1 mol) dodecyl bromide are heated in the presence of 4 g. sodium bromide at 170° C. for 15 hours while stirring. After working up in the usual manner, there are obtained 20 g. (0.06 mol) ethane-phosphonic acid-O-isopropyl-O-dodecyl ester.

EXAMPLE 10

278 grams (1 mol) dodecane-phosphonic acid dimethyl ester and 184 g. (1 mol) butyl iodide are heated in the presence of 6 g. sodium iodide at 130° C. for 10 hours while stirring. After working up in the usual manner, there are obtained 86 g. (0.26 mol) dodecane-phosphonic acid-O-methyl-O-butyl ester.

EXAMPLE 11

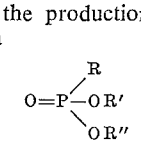
186 grams (1 mol) benzene-phosphonic acid dimethyl ester and 137 g. (1 mol) butyl bromide are heated in the presence of 4 g. sodium bromide at 130° C. for 20 hours while stirring. After working up in the usual manner, there are obtained 64 g. (0.3 mol) benzene-phosphonic acid-O-methyl-O-butyl ester of refractive index n_D^{20} 1.4898.

EXAMPLE 12

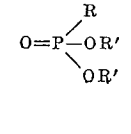
212 grams (1 mol) 2-phenyl-ethylene-phosphonic acid dimethyl ester and 137 g. (1 mol) butyl bromide are heated in the presence of 4 g. sodium bromide at 120–130° C. for 12 hours while stirring. After working up in the usual manner, there are obtained 60 g. (0.23 mol) 2-phenyl-ethylene-phosphonic acid-O-methyl-O-butyl ester.

I claim:

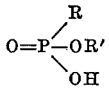
1. A process for the production of phosphonic acid esters of the formula



wherein R stands for a hydrocarbon radical containing 1–18 carbon atoms, R′ stands for an alkyl radical containing 1–3 carbon atoms and R″ stands for an alkyl or aralkyl radical containing 4–18 carbon atoms or for an alkenyl radical containing 3–18 carbon atoms comprising reacting at a temperature from 80 to 150° C. phosphonic acid diesters of the formula



wherein R and R′ have the above meaning with a halide of the formula R″X wherein R″ has the above meaning and X stands for chlorine, bromine or iodine in the presence of alkali metal, alkaline earth metal or ammonium salts of hydrohalic acids or partially esterfied phosphonic acids of the formula



wherein R and R′ have the above meaning

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