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ESTERS OF PARAFFIN PHOSPHONIC ACIDS

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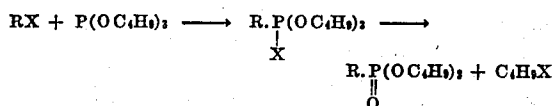
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The present invention relates to esters of paraffin phosphonic acids and more particularly to the dibutyl esters of paraffin phosphonic acids and to a method of producing the same.

Dibutyl paraffin phosphonates are of commercial interest in the preparation of paraffin phosphonic acids, the dibutyl esters being more readily isolated than esters of the phosphonic acids with the lower alcohols and more easily hydrolyzed than esters of the phosphonic acids with the higher alcohols. Since higher alkane phosphonic acids or their ammonium or alkali metal salts possess very good surface active properties, the dibutyl esters of phosphonic acids of from, say, 8 to 18 carbon atoms, are particularly useful as intermediates in the production of wetting-out agents, detergents, etc. Dibutyl esters of such higher alkane phosphonic acids are also advantageously employed as additives to lubricants for the purpose of modifying viscosity and at the same time imparting extreme pressure resistance to the same. The higher alkane esters, i. e., the dibutyl esters of paraffin phosphonic acids having at least 8 carbon atoms, but less than 19 carbon atoms in the acid portion of the molecule, are particularly valuable as plasticizers for resinous materials. Certain of the esters have the property of imparting a substantially permanent softening effect to fibrous materials.

As far as I have been able to ascertain, the only method which has been heretofore employed for the preparation of the dibutyl esters is that disclosed by Arbuzov and Arbuzova (J. Russ. Phys.-Chem. Soc. 62, 1933 (1930)), wherein there is reported the preparation of dibutyl n-butane phosphonate by reaction of tributyl phosphite with n-butyl iodide. The reaction was conducted in a sealed tube at a temperature of about 150° C. and the phosphonate was obtained in a yield of about 58%. When attempting to prepare the higher alkane phosphonates employing alkyl halides of 6 or more carbon atoms by the method disclosed by Arbuzov et al., the reaction was found to be so sluggish as to make this process of no economic value. The production of the higher dibutyl paraffin phosphonates is further complicated by the fact that all of the intermediate addition product does not decompose during the reaction:



In the above reaction X is a halogen. The diffi-

culty with which the intermediate phosphonium compound is formed and decomposed appears to be directly responsible for the low yields. The presence of the phosphonium compound in the reaction mixture has also a further disadvantage. During fractionation, for isolation of the dibutyl paraffin phosphonate, the presence of the intermediate phosphonium compound appears to lead to troublesome decomposition of the desired product, even at oil-pump vacua (2 or 3 mm. Hg).

Accordingly, the Arbuzov et al. method, referred to above, could not be used for the commercial preparation of higher paraffin phosphonates, i. e., for the dibutyl esters of paraffin phosphonic acids in which hydrocarbon radical contains at least six carbon atoms.

Another known method for the preparation of esters of certain paraffin phosphonic acids involves the reaction of sodium diethyl phosphite and an alkyl halide. The diethyl esters of methanephosphonic acid, ethanephosphonic acid, propanephosphonic acid and butanephosphonic acid have been prepared in this manner. Because sodium diethyl phosphite is insoluble in most inert organic liquids, except ether, this method presents difficulties in that it is almost imperative to use hot anhydrous ether as solvent, which material also colloiddally disperses some of the sodium halide generated by the reaction. The commercial use of ether as a solvent is also undesirable because of the fire hazard and because of the difficulty encountered in maintaining anhydrous conditions when operating on a commercial scale. The use of sodium diethyl phosphite is additionally complicated by the fact that the hygroscopicity of this ester prohibits its ready handling except in specially designed equipment. Also, the diethyl phosphonates were found to be separable from the reaction products only with difficulty because their susceptibility to hydrolysis prevents washing out the sodium halide with water; hence, separation of the diethyl phosphonates necessitates centrifuging for the removal of the colloiddally dispersed sodium halide. In many instances even prolonged centrifuging was found to be ineffective for complete removal of the inorganic salt. These older methods were, therefore, suitable for laboratory preparations only.

Now I have found that when sodium dibutyl phosphite, instead of sodium diethyl phosphite, is employed for the preparation of esters of paraffin phosphonic acids, the above disadvantages are obviated. Reaction may conveniently be effected in such relatively high boiling solvents such as hexane, xylene, toluene, petroleum ether or ben-

zene. Sodium dibutyl phosphite is substantially non-hygroscopic; hence, no special precautions need be observed in its preparation, handling and storage. The resulting dibutyl paraffin phosphonates are not hydrolyzed by washing with water; consequently, the by-product, sodium halide, can readily be removed therefrom simply by washing the reaction product with water. The present method, involving the reaction of sodium dibutyl phosphite and any alkyl halide for the preparation of dibutyl paraffin phosphonates, enables the production of the dibutyl phosphonates in yields varying from, say, 75% to 95% over a period of a few hours at temperatures of from room temperature to 150° C. without the necessity of employing pressure vessels. These results, as has been stated above, are not obtainable when working with tributyl phosphite.

In preparing the dibutyl paraffin phosphonates according to the present invention, I prefer to operate substantially as follows: Approximately molecular equivalents of sodium dibutyl phosphite and an alkyl halide, i. e., an alkyl bromide, iodide or chloride, are mixed together in an inert solvent at temperatures between room temperature to 150° C., until separation of sodium halide is substantially complete. The initially separated sodium halide appears in colloidal form; however, due to the conditions of reaction employed, the colloidal sodium halide rapidly coalesces to the crystalline form which readily separates from the reaction mixture. Accordingly, the endpoint can readily be observed by momentarily discontinuing the agitation, and noting the clarity of the reaction mixture. Cloudiness of the reaction mixture, due to the presence of colloidal particles of sodium halide, therefore, shows that the reaction is incomplete. At the end of the condensation there is evidenced a clear separation of the crystalline sodium halide from the other reaction constituents, the sodium halide settling to the bottom of the reaction mixture and the supernatant liquid being essentially unclouded. Substantially complete separation of the sodium halide usually takes place within a period of from 2 to 3 hours, although for the preparation of the higher paraffin phosphonates a somewhat longer reaction time is desirable. When employing refluxing temperatures, even with the C₁₈ and C₁₈ halides, a period of from 5 to 6 hours generally is sufficient for complete reaction. The temperature employed for the reaction varies with the nature of the alkyl halide employed as well as with the reaction time. With the lower alkyl halides lower temperatures are advantageously employed; for example, for the preparation of dibutyl methanephosphonate, reaction is effected simply by stirring together at room temperature in an inert solvent substantially equimolar quantities of sodium dibutyl phosphite and a methyl halide. With the higher alkyl halides, refluxing temperatures at atmospheric pressure are advantageously employed.

Upon complete separation of sodium halide from the reaction mixture, i. e., at the end of the reaction, the mixture is allowed to attain room temperature if heating has been employed, and is then washed thoroughly with water in order to remove the sodium halide. The organic layer is then separated, the solvent is removed from the organic layer by distillation under reduced pressure, and the residue then distilled in vacuo in a fractionating apparatus. One fractionation generally yields the dibutyl paraffin phosphonate in substantially pure form. The

solvent employed may be hexane, heptane, petroleum ether, xylene, benzene, toluene or any other liquid which is a solvent for both the sodium dibutyl phosphite and the alkyl halide and is inert under the reaction conditions. When working with those alkyl halides which are liquids, there may be employed an excess of the alkyl halide instead of the inert solvent or diluent, the alkyl halide itself serving as the solvent. In this case reaction may also be carried out in the absence of either an excess of alkyl halide or an inert solvent, equimolar quantities merely being stirred together at ordinary or increased temperatures, i. e., at temperatures of up to 150° C.

The present invention thus provides a highly efficient method for the production of dibutyl esters of paraffin phosphonic acids having from 1 to 18 carbon atoms. The present invention also provides for industry a series of highly valuable, stable, phosphorus-containing organic compounds, i. e., the dibutyl esters of paraffin phosphonic acids of from 8 to 18 carbon atoms. These esters differ from the known dibutyl butanephosphonic acid in that they are readily converted to free, higher paraffin phosphonic acids or their salts, which materials are highly useful in surface-active compositions. The present dibutyl higher paraffin phosphonic esters are advantageously employed as plasticizers, lubricant additives and textile-softening compounds.

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

Example 1

Preparation of sodium dibutyl phosphite.—Metallic sodium (4.6 g.; 0.2 atom) was placed into a three-necked round bottom flask, provided with a dropping funnel, a sealed stirrer and a reflux condenser closed with a calcium chloride tube; 300 cc. of dry hexane was placed into the flask and, while the liquid was being gently refluxed with agitation, dibutyl phosphite (39.0 g.; 0.2 mol) was added dropwise during a period of from 20 to 30 minutes, after which the refluxing and stirring were continued until the sodium was completely dissolved.

Preparation of dibutyl n-hexanephosphonate.—To the sodium dibutyl phosphite, prepared as described above, there was added 33 g. (0.2 mol) of n-hexyl bromide during a period of from 30 to 45 minutes and the mixture was stirred with gentle reflux for 5 to 6 hours. Separation of sodium bromide generally began after 15 to 20 minutes and was completed in about six hours. The reaction mixture was then allowed to stand overnight and washed thoroughly with water. The organic layer was then subjected to distillation under reduced pressure for removal of the solvent and any unreacted materials. Fractionation gave 52 g. (93% yield) of substantially pure dibutyl n-hexanephosphonate, B. P. 182–184° C./20 mm., n_D^{25} 1.4332, d_4^{25} 0.9366.

Hydrolysis of dibutyl n-hexanephosphonate by refluxing 50 g. of the same with 100 cc. of concentrated hydrochloric acid for a time of approximately 15 hours gave substantially a 100% theoretical yield of crude n-hexanephosphonic acid; the pure compound, M. P. 104.5° C. to 106° C. was obtained by recrystallization of the crude product.

Following the procedure described above for the preparation of dibutyl n-hexanephosphonate, but using other n-alkyl bromides instead of n-hexyl bromide, there was obtained the series of

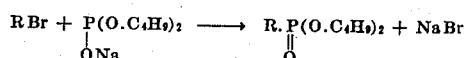
dibutyl paraffin phosphonates shown in the table which follows:

Example 2

This example shows the employment of dibutyl

Dibutyl alkane phosphonate	Boiling point,		n_D^{20}	d_4^{20}	MR		Yield, percent
	° C.	Mm.			Obs.	Calc.	
Ethane.....	137-9	17	1.4258	0.9823	59.09	59.13	78
n-Butane.....	160-2	20	1.4302	0.9462	68.28	68.4	86
n-Pentane.....	167-9	17	1.4318	0.9428	72.60	72.98	88
n-Hexane.....	182-4	20	1.4332	0.9386	77.17	77.60	93
n-Heptane.....	188-90	17	1.4355	0.9313	82.20	82.22	73
n-Octane.....	147-8	2	1.4370	0.9262	86.56	86.84	75
n-Nonane.....	159-61	2	1.4391	0.9253	90.98	91.45	69
n-Decane.....	161	1	1.4402	0.9232	95.37	96.05	80
n-Dodecane.....	196-9	3	1.4432	0.9153	104.9	105.3	75
n-Tetradecane.....	217-9	3	1.4460	0.9114	114.1	114.55	75
n-Hexadecane.....	226-8	2	1.4481	0.9090	123.2	123.8	85
n-Octadecane.....	248-50	2	1.4499	0.9037	132.6	133.02	75

The dibutyl paraffin phosphonates shown in the above table were obtained according to the reaction:



I have found that R may be any alkyl radical of from 1 to 18 carbon atoms, branched or unbranched, i. e., methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl n-amyl, isoamyl n-hexyl, 2-ethylbutyl, n-heptyl, n-octyl, iso-octyl, 2-ethylhexyl, n-nonyl, iso-nonyl, n-decyl, n-undecyl, n-dodecyl, etc. I have also found that primary alkyl halides are more reactive in the condensation than are the secondary alkyl halides. Accordingly, the primary alkyl halides are preferred in the present reaction. Instead of employing alkyl bromides, I may use the corresponding alkyl iodides or the corresponding alkyl chlorides. However, the alkyl chlorides do not participate in the reaction as readily as do the iodides and the bromides, and accordingly, when using the alkyl chlorides somewhat longer reaction periods and higher temperatures are required than when the alkyl halide is an iodide or bromide.

The dibutyl paraffin phosphonates are readily hydrolyzed by treatment with concentrated hydrochloric acid in an open vessel to yield the corresponding paraffin phosphonic acids. Employing the procedure shown above for the preparation of n-hexanephosphonic acid, the following paraffin phosphonic acids were obtained in a high degree of purity:

Paraffin phosphonic acid	Melting point, °C.
Ethane.....	61-2
n-Butane.....	103.4-4
n-Pentane.....	120.5-1.5
n-Hexane.....	104.5-6
n-Heptane.....	103-3.5
n-Octane.....	99.5-100.5
n-Nonane.....	99-100
n-Decane.....	102-2.5
n-Tetradecane.....	100.5-1.5
n-Hexadecane.....	97-8
n-Octadecane.....	94.5-5.5
	98.5-9.0

The present method for the preparation of dibutyl paraffin phosphonates thus provides a commercial, economically feasible process for the manufacture of the individual, substantially pure paraffin phosphonic acids, these free acids being obtainable in substantially quantitative yields by hydrolysis of the dibutyl esters. Of these free acids, those having from 10 to 16 carbon atoms, or the alkali metal salts of such acids, are highly valuable as deterative and wetting-out agents.

tetradecanephosphonate as a plasticizer for various synthetic resinous materials. The following solutions of the resins were prepared:

1. A solution consisting of 10 parts by weight of a polyvinyl butyral resin known as "Butvar" and 90 parts by weight of ethyl alcohol.

2. A solution consisting of 10 parts by weight of ethyl cellulose and 90 parts by weight of xylene.

3. A solution consisting of 20 parts by weight of nitrocellulose and 80 parts by weight of a mixture consisting of 40% of butyl acetate, 20% of ethyl acetate, 10% of ethyl alcohol and 30% of toluol.

4. A solution consisting of 50 parts by weight of pentaerythritol-phthalic anhydride alkyd resin which had been modified with 60% linseed oil and 50 parts by weight of mineral spirits.

To each of the above solutions there was added an amount of dibutyl tetradecanephosphonate which was equivalent to 20% by weight of the weight of the solid resin. The ester dissolved readily without residue into each of the solutions. Films cast from each of the ester-containing solutions were clear, transparent and brilliant. They possessed a high degree of flexibility and toughness. Similar improved results may be obtained by any of the dibutyl alkane phosphonates having from 8 to 18 carbon atoms in the acid portion of the molecule. Dibutyl butane phosphonates are not suitable for this purpose.

Example 3

Desized cotton fabric was impregnated to the extent of 5 per cent by weight with dibutyl decanephosphonate, a hexane solution of the ester being employed as the impregnating medium. The resulting dried, treated cloth showed an improvement in both feel and hand.

While the invention has been described with particular reference to specific embodiments, it is to be understood that it is not to be limited thereto but is to be construed broadly and restricted solely by the scope of the appended claims.

What I claim is:

1. The process for preparing dibutyl esters of alkane phosphonic acids which comprises mixing together an alkyl halide and sodium dibutyl phosphite until sodium halide has separated therefrom, removing the separated sodium halide and then distilling the mixture to recover a dibutyl alkane phosphonate.

2. The process for preparing dibutyl esters of alkane phosphonic acids which comprises mixing together an alkyl halide and sodium dibutyl phosphite, heating said mixture until sodium halide has separated therefrom, removing the

separated sodium halide from the mixture and then distilling the mixture to recover a dibutyl alkane phosphonate.

3. The process for preparing dibutyl esters of alkane phosphonic acids which comprises mixing together an alkyl halide and sodium dibutyl phosphite, heating said mixture while agitating the same until sodium halide has separated therefrom, washing said mixture with water to remove sodium halide and then distilling the residue to recover a dibutyl alkane phosphonate.

4. The process for preparing dibutyl esters of alkane phosphonic acids which comprises mixing together an alkyl halide and sodium dibutyl phosphite, heating said mixture while agitating the same until sodium halide has separated therefrom, filtering said mixture to remove separated sodium halide and then distilling the filtrate to recover a dibutyl alkane phosphonate.

5. The process for preparing dibutyl esters of alkane phosphonic acids which comprises mixing together a primary alkyl halide and sodium dibutyl phosphite, separating a solid phase of sodium halide therefrom and then distilling the mixture to recover a dibutyl alkane phosphonate.

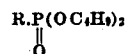
6. The process for preparing dibutyl esters of alkane phosphonic acids which comprises mixing together a primary alkyl bromide and sodium dibutyl phosphite, separating the solid phase of sodium bromide therefrom and then distilling the mixture to recover a dibutyl alkane phosphonate.

7. The process for preparing dibutyl decane phosphonate which comprises heating a mixture of n-decane bromide and sodium dibutyl phosphite, separating crystalline sodium bromide from the reaction mass and then distilling the organic residue to recover dibutyl decane phosphonate.

8. The process for preparing dibutyl dodecane phosphonate which comprises heating a mixture of dodecane bromide and sodium dibutyl phosphite, separating crystalline sodium bromide from the reaction mass and then distilling the organic residue to recover dibutyl dodecane phosphonate.

9. The process for preparing dibutyl tetradecane phosphonate which comprises heating a mixture of tetradecane bromide and sodium dibutyl phosphite, separating crystalline sodium bromide from the reaction mass and then distilling the organic residue to recover dibutyl tetradecane phosphonate.

10. Dibutyl alkane phosphonates of the formula:



where R is an alkane radical having at least 8 carbon atoms but less than 19 carbon atoms.

11. Dibutyl decane phosphonate.

12. Dibutyl dodecane phosphonate.

13. Dibutyl tetradecane phosphonate.

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