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2,961,454

ESTER INTERCHANGE

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6 Claims. (Cl. 260-461)

This invention relates to the preparation of esters of phosphorous acid.

It is an object of the present invention to develop an improved process for preparing tertiary phosphites of high boiling alcohols.

Another object is to prepare such phosphites having improved physical properties and particularly having improved purity.

A further object is to prepare novel phosphites.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by transesterification of tris 2-chlorpropyl phosphite with a higher boiling monohydric or polyhydric alcohol.

Preferably, tris 2-chlorpropyl phosphite is employed.

In place of tris 2-chlorpropyl phosphite, less preferably there can be employed tris 2-chlorbutyl phosphite.

As the higher boiling monohydric alcohol there are employed alcohols having higher boiling points than propylene chlorhydrin. Among such alcohols are alkanols and cycloalkanols, such as n-hexanol, n-heptanol, n-octanol, 2-ethyl hexanol, isooctyl alcohol, octanol-2, 2-methyl heptanol-2, n-decyl alcohol, isodecyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, cyclohexanol, methyl cyclohexanol, alkanediols or glycols such as ethylene glycol, propylene glycol, trimethylene glycol, 1,2-butylene glycol, 2,3-butylene glycol, 1,4-butylene glycol, 1,6-hexanediol, pinacol, 1,2-pentanediol, 2-methyl-2,4-pentanediol, 1,3-butylene glycol, neopentyl glycol, 2-ethyl-1,3-hexanediol, 2,4-pentanediol, 2,4-heptanediol, 2,2-diethyl-1,3-propanediol, 2-ethyl-2n-butyl-1,3-propanediol, and also pentaerythritol.

The present invention is particularly valuable in preparing the tris alkyl phosphites from alkanols having 6 to 12 carbons.

The transesterification between the tris 2-chlorpropyl phosphite and the alcohol can be carried out at any temperature from room temperature to the boiling point of propylene chlorhydrin, at the pressure employed. Thus, at atmospheric pressure the reaction can be carried out at temperatures up to 133° C. The reaction can be carried out at atmospheric, or subatmospheric pressure. Preferably, the pressure is subatmospheric, e.g., 50 mm. or less. The propylene chlorhydrin formed is distilled off and the desired phosphite is recovered as the residue from such distillation.

It is also possible to carry out the reaction at atmospheric pressure and then separate the desired phosphite ester from the propylene chlorhydrin formed by distillation at reduced pressure, e.g., 25 mm. or less.

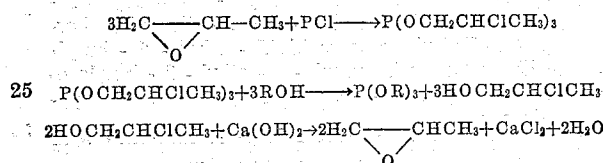
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One of the advantages of the present process is that no catalyst need be employed and, hence, there is no need to remove the catalyst from the product. The present procedure is also cheaper than the conventional routes for forming alkyl phosphites.

The propylene chlorhydrin by-product formed in the transesterification has a boiling point which is 50° C. Lower than the boiling point of phenol. Hence, the products can be isolated at a lower temperature than when using triphenyl phosphite as the transesterifying agent. Additionally, when using triphenyl phosphite, an alkaline catalyst is employed.

The products obtained according to the present invention, e.g., the tris higher alkyl phosphites, are water white and are of an excellent purity. In this respect they are superior to the same phosphites prepared using present commercial procedures or tri 2-chlorethyl phosphite as the transesterifying agent.

On a commercial basis the overall reaction is as follows:



R in the formulae stands for the alkyl group. It is thus evident that the propylene oxide starting material can be continuously regenerated.

The use of tris 2-chlorpropyl phosphite over tris 2-chlorethyl phosphite has the advantage that propylene oxide is easier to handle than ethylene oxide. In addition, the by-product propylene chlorhydrin formed in the transesterification is less toxic than the by-product ethylene chlorhydrin. Furthermore, it has been found that the products made from tris chlorpropyl phosphite interesterification are easier to control and work up and have reduced acid numbers (the acid number indicates the residual acid in the product). For example, tri n-decyl phosphite prepared from tris 2-chlorethyl phosphite and n-decyl alcohol had an acid number of 5-10, whereas when tris 2-chlorpropyl phosphite was used as the transesterifying agent, the acid number was 0.02-0.5.

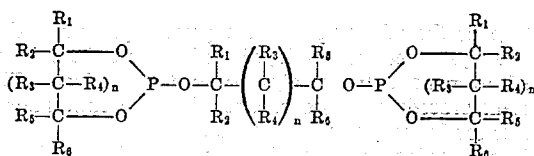
In order to insure complete ester interchange using a monohydric alcohol there should be employed at least 3 moles of the alcohol per mole of the tris 2-chlorpropyl phosphite. Generally, from 1-15% molar excess of the alcohol is employed to insure formation of the trialkyl ester. No advantage has been found in using over 15% excess alcohol and, in general, 10-15% excess of the alcohol gives the best commercial quality product. The use of larger amounts of the alcohol means that more alcohol must be recovered in the subsequent distillation.

If less than three moles of the monohydric alcohol are employed then mixed phosphites are obtained. Thus when 2 moles of the monohydric alcohol are employed per mole of tris 2-chlorpropyl phosphite there are obtained compounds such as diceryl 2-chlorpropyl phosphite, distearyl 2-chlorpropyl phosphite, dimethyl 2-chlorpropyl phosphite. Where one mol of monohydric alcohol is employed per mole of tris 2-chlorpropyl phosphite there are obtained compounds such as hexyl di-2-chlorpropyl phosphite, stearyl di-2-chlorpropyl phosphite, methyl di-2-chlorpropyl phosphite, and decyl di-2-chlorpropyl phosphite.

When using α,β or α,γ glycols, if one equivalent (or more) of polyhydric alcohol is used per equivalent of tris 2-chlorpropyl phosphite (e.g., 3 moles of ethylene

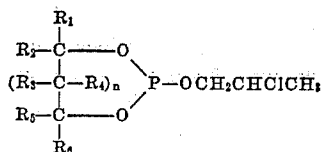
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glycol with 2 moles of 2 chlorpropyl phosphite) there are formed products of the following type:



where R_1, R_2, R_3, R_4, R_5 , and R_6 are hydrogen or lower alkyl and n is 0 or 1. Examples of such compounds are bis (4,4,6-trimethyl - 1,3,2 - dioxaphosphorinanoxy) 1,1,3 propane; bis(1,3,2-dioxaphospholanoxy) ethane; bis(4-methyl - 1,3,2 - dioxaphospholanoxy) - 1 - methylethane; bis(4,5 - dimethyl - 1,3,2 - dioxaphospholanoxy) - 1 - ethylethane; bis(4,4,5,5 - tetramethyl - 1,3,2 - dioxaphospholanoxy) 1,1,2,2 tetramethylethane; bis(4 - propyl - 1,3,2 - dioxaphosphorinanoxy) - 1 - proylethane; bis(1,3,2-dioxaphosphorinanoxy) propane; bis(4 - methyl - 1,3,2 - dioxaphosphorinanoxy) - 1 - methylpropane; bis(5,5-dimethyl - 1,3,2 - dioxaphosphorinanoxy)-2,2-dimethylpropane; bis(4 propyl - 5 - ethyl - 1,3,2 - dioxaphosphorinanoxy) - 1 - propyl - 2 - ethylpropane; bis(4 - propyl - 6 - methyl - 1,3,2 dioxaphosphorinanoxy) - 1 - propyl - 3 - methylpropane; bis(5,5-diethyl - 1,3,2 - dioxaphosphorinanoxy)-2,2-diethyl propane; bis(5 - ethyl - 5 - butyl - 1,3,2 - dioxaphosphorinanoxy) - 2 - ethyl - 2 - butylpropane; and bis(4-propyl - 1,3,2 - dioxaphosphorinanoxy)-1-propylpropane.

If less than one equivalent of diol is employed then monomeric products are formed which still have a chlorpropyl group. Thus, when reacting one mol of tris 2-chlorpropyl phosphite with one mol (or less) of a diol having 2 to 3 carbon atoms separating the hydroxyl groups, there are formed products of the formula:



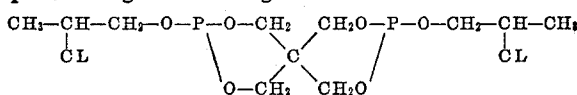
where R_1, R_2, R_3, R_4, R_5 and R_6 are hydrogen or lower alkyl and n is either 0 or 1. Examples of compounds coming within this formula are 2-(2-chloro)propyl 1-4,4,6-trimethyl-1,3,2 - dioxaphosphorinane; 2 - (2 - chloro)propoxy - 1,3,2 - dioxaphospholane; 2 - (2 - chloro)propoxy - 4 - methyl - 1,3,2 - dioxaphospholane; 2 - (2 - chloro)propoxy - 4,5 - dimethyl - 1,3,2 - dioxaphospholane; 2-(2 - chloro)propoxy - 4 - ethyl - 1,3,2 - dioxaphospholane; 2-(2 - chloro)propoxy - 4,4,5,5 - tetramethyl - 1,3,2 - dioxaphospholane; 2 - (2 - chloro)propoxy - 4 - propyl - 1,3,2 - dioxaphospholane; 2-(2-chloro)propoxy - 1,3,2 - dioxaphosphorinane; 2 - (2 - chloro)propoxy - 4 - methyl - 1,3,2 - dioxaphosphorinane; 2-(2-chloro)propoxy - 5,5 - dimethyl - 1,3,2 - dioxaphosphorinane; 2 - (2 - chloro)propoxy 4-propyl - 5 - ethyl - 1,3,2-dioxaphosphorinane; 2 - (2 - chloro)propoxy - 4 - propyl-6-methyl - 1,3,2 - dioxaphosphorinane; 2 - (2 - chloro)propoxy - 5,5 - diethyl - 1,3,2 - dioxaphosphorinane; 2 - (2-chloro)propoxy - 5 - ethyl - 5-butyl-1,3,2-dioxaphosphorinane; 2-(2-chloro)propoxy - 5 - ethyl - 5-butyl - 1,3,2 - dioxaphosphorinane; 2-(2-chloro)propoxy-4-propyl-1,3,2-dioxaphosphorinane.

The compounds containing a 2-chlorpropoxy group and a 5 or 6 member heterocyclic ring are new compounds as are the compounds having two heterocyclic rings joined through an oxyalkyleneoxy bridge. They are useful as stabilizers and plasticizers for vinyl chloride resins and other plastics. They are also useful as insecticides. The other tertiary phosphites disclosed likewise are useful as plasticizers and stabilizers for vinyl chloride resins.

When 2 mols of tris 2-chlorpropyl phosphite are reacted with 1 mol of pentaerythritol there is formed a

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spiro compound bis 2 chlorpropyl pentaerythritol diphosphite having the following formula:



This compound is useful as any intermediate for forming polymers which can be molded to form cups, etc. and is also useful as a vinyl chloride resin plasticizer.

Unless otherwise stated, all parts and percentages are by weight.

Example 1

311 grams (1 mol) of tris 2-chlorpropyl phosphite were mixed with 534 grams (3 moles +12.7% excess) of isodecyl alcohol. The mixture was then distilled in a vacuum at 10-15 mm. until the pot temperature was 150° C. The triisodecyl phosphite recovered from the pot was water white, had an acid number well below 0.5 an N_D^{25} of 1.4540 and a d^{25} of 0.898.

Example 2

Example 1 was repeated utilizing 534 grams of n-decyl alcohol in place of the isodecyl alcohol. There was obtained tri n-decyl phosphite in excellent yields.

Example 3

	Moles
Tris 2-chlorpropyl phosphite	1
n-Octanol	3

The process of Example 1 was repeated and there was recovered tri n-octyl phosphite of excellent purity.

Example 4

	Moles
Tris 2-chlorpropyl phosphite	1
2-ethylhexanol	3.4

The process of Example 1 was repeated and the tri 2-ethylhexyl phosphite recovered as a water white liquid had the following properties: N_D^{25} 1.4489; d^{25} 0.915.

Example 5

	Moles
Tris 2-chlorpropyl phosphite	1
Isooctyl alcohol	3.3

The process of Example 1 was repeated and triisooctyl phosphite was recovered.

Example 6

	Moles
Tris 2-chlorpropyl phosphite	1
n-Hexyl alcohol	3.3

The process of Example 1 was repeated and tri n-hexyl phosphite was recovered.

Example 7

	Moles
Tris 2-chlorpropyl phosphite	1
Cyclohexanol	3.2

The process of Example 1 was repeated and tricyclohexyl phosphite was recovered.

Example 8

	Moles
Tris 2-chlorpropyl phosphite	1
Lauryl alcohol	3.3

The process of Example 1 was repeated and trilauryl phosphite was recovered.

Example 9

	Moles
Tris 2-chlorpropyl phosphite	1
Stearyl alcohol	3.3

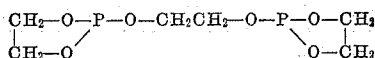
The process of Example 1 was repeated and tri stearyl phosphite was recovered.

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Example 10

Tris 2-chloropropyl phosphite.....	Moles
Ethylene glycol.....	3

The process of Example 1 was repeated and bis (1,3,2 dioxaphospholanoxo) ethane having the formula



was recovered.

Example 11

Tris 2-chloropropyl phosphite.....	Moles
Decyl alcohol.....	2

The process of Example 1 was repeated and there was recovered di decyl 2-chloropropyl phosphite.

Example 12

Tris 2-chloropropyl phosphite.....	Moles
Pinacol.....	3

The process of Example 10 was repeated and there was recovered bis (4,4,5,5-tetramethyl, 1,3,2-dioxaphospholanoxo)-1,1,2,2-tetramethylethane.

Example 13

Tris 2-chloropropyl phosphite.....	Moles
2-methyl-2,4-pentanediol.....	3

The process of Example 10 was repeated and there was recovered bis (4,4,6-trimethyl-1,3,2-dioxaphosphorinanoxo) 1,1,3-trimethylpropane.

Example 14

Tris 2-chloropropyl phosphite.....	Moles
Decyl alcohol.....	1

The process of Example 1 was repeated and there was recovered decyl di-2-chloropropyl phosphite.

Example 15

Tris chlorpropyl phosphite.....	Moles
Stearyl alcohol.....	1

The process of Example 1 was repeated and there was recovered stearyl di-2-chloropropyl phosphite.

Example 16

Tris 2-chloropropyl phosphite.....	Moles
Stearyl alcohol.....	2

The process of Example 1 was repeated and there was recovered di stearyl 2-chloropropyl phosphite.

Example 17

Tris 2-chlorobutyl phosphite.....	Moles
2-ethylhexanol.....	3.3

The process of Example 1 was repeated and there was recovered tri 2-ethylhexyl phosphite as the still residue.

Example 18

Tris 2-chlorobutyl phosphite.....	Moles
n-Decyl alcohol.....	3.2

The process of Example 1 was repeated and there was recovered tri decyl phosphite as the still residue.

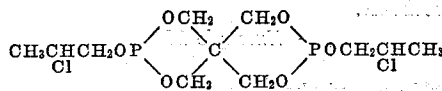
Example 19

Tris 2-chloropropyl phosphite.....	Moles
Pentaerythritol.....	1

The process of Example 1 was repeated and there was

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recovered bis (2-chloropropoxy) spiro 1,3,2 phosphorinane having the formula:

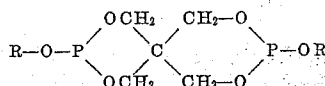


as a very viscous, slightly yellow liquid N_D^{25} 1.5012, d_4^{20} 1.355.

Example 20

Compound of Example 19.....	Moles
Decyl alcohol.....	2

The process of Example 1 was repeated and there was recovered didecyl pentaerythritol diphosphite as an almost colorless viscous liquid N_D^{25} 1.4731, d_4^{25} 1.030. By replacing the decyl alcohol in Example 20 by stearyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol or lauryl alcohol the corresponding dialkyl pentaerythritol diphosphites having the general formula:



where R is an alkyl group are obtained. These materials can be used as plasticizers for vinyl chloride resins.

Example 21

Tris 2-chloropropyl phosphite.....	Moles
1,2-propanediol.....	1

The process of Example 1 was repeated and there was discovered 2-(2-chloro) propyl-4-methyl-1,3,2-dioxaphospholane.

Example 22

Tris 2-chloropropyl phosphite.....	Moles
1,3-propanediol.....	1

The process of Example 1 was repeated and there was recovered 2-(2-chloro) propyl-1,3,2-dioxaphosphorinane.

Example 23

Tris 2-chloropropyl phosphite.....	Moles
2,3 butanediol.....	1

The process of Example 1 was repeated and there was recovered 2-(2-chloro) propyl-4,5-dimethyl-1,3,2-dioxaphospholane.

Example 24

Tris 2-chloropropyl phosphite.....	Moles
Ethylene glycol.....	1

The process of Example 1 was repeated and there was recovered 2-(2-chloro) propyl-1,3,2 dioxaphospholane.

Example 25

Tris 2-chloropropyl phosphite.....	Moles
Neopentyl glycol.....	1

The process of Example 1 was repeated and there was recovered 2-(2-chloro) propyl-5,5-dimethyl-1,3,2-dioxaphospholane.

Example 26

Tris 2-chloropropyl phosphite.....	Moles
Butanediol-1,3.....	1

The process of Example 1 was repeated and there was recovered 2-(2-chloro) propyl-4-methyl-1,3,2-dioxaphosphorinane.

Example 27

Tris 2-chloropropyl phosphite.....	Moles
2,2-dimethyl propanediol-1,3.....	1

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The process of Example 1 was repeated and there was recovered 2-(2-chloro) propyl-5,5-dimethyl-1,3,2-dioxaphosphorinane.

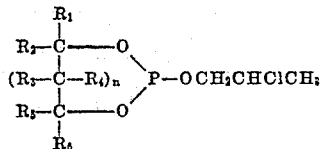
Example 28

Tris 2-chloropropyl phosphite-----	1
2-ethyl-2-n-butyl-1,3-propanediol -----	1

The process of Example 1 was repeated and there was recovered 2-(2-chloro) propyl-5-ethyl-5-butyl-1,3,2-dioxaphosphorinane.

What is claimed is:

1. Cyclic phosphites having the formula

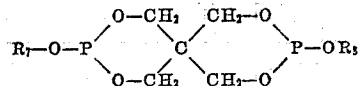


where R_1 , R_2 , R_3 , R_4 , R_5 and R_6 are selected from the group consisting of hydrogen and lower alkyl groups,

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and n is an integer of the group consisting of 0 and 1.

2. Cyclic phosphites having the formula



wherein R_7 and R_8 are selected from the group consisting of alkyl having 6 to 18 carbon atoms in the alkyl group and 2 chloropropyl.

3. A compound according to claim 2 wherein both R_7 and R_8 are decyl.

4. A compound according to claim 2 wherein both R_7 and R_8 are stearyl.

5. A compound according to claim 2 wherein R_7 and R_8 are both lauryl.

6. Bis (4,4,6-trimethyl-1,3,2-dioxaphosphorinanoxy) 1, 1,3-trimethyl propane.

References Cited in the file of this patent**UNITED STATES PATENTS**

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Notice of Adverse Decision in Interference

In Interference No. 93,252 involving Patent No. 2,961,454, H. Gould and J. P. Rakus, Ester interchange, final decision adverse to the patentees was rendered Aug. 21, 1963, as to claim 3.

[Official Gazette November 12, 1963.]