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METHOD FOR PREPARING MIXED ALKYL ESTERS OF PHOSPHORIC ACID

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1

This invention relates to the preparation of neutral esters of phosphoric acid in which the alkyl groups differ by reacting upon a trialkyl phosphate or an alkyl pyrophosphate or an alkyl metaphosphate with an alkyl chlorosulfinate or an alkyl chloroformate, the chlorosulfinate or chloroformate having different alkyl groups than the alkyl phosphate.

Hull and Snodgrass in their Patent No. 2,407,279 have described a method for preparing trialkyl phosphates in an economical manner by the reaction of P_2O_5 with diethyl ether. Also, alkyl pyrophosphates or alkyl metaphosphates can be obtained as other products of this reaction. However, the method described in the prior art for replacing one or two or more of the alkyl groups of a trialkyl phosphate with other alkyl groups is through alcoholysis. For instance, by the alcoholysis of triethyl phosphate with butyl alcohol, ethyl dibutyl phosphate or dibutyl ethyl phosphate may be obtained. This method, however, is accompanied by the simultaneous formation of substantial quantities of mixed alkyl ethers and alkyl phosphoric acids, resulting in very low yields of the described phosphate esters.

One object of my invention is to provide a method for replacing the alkyl groups of a trialkyl phosphate with other alkyl groups by a method giving a substantially better yield than has been previously obtained. Another object of my invention is to replace the alkyl groups of a trialkyl phosphate with the alkyl groups of an alkyl chlorosulfinate or chloroformate. Other objects of my invention will appear herein.

I have found that one, two or even all of the alkyls of a trialkyl phosphate can be replaced by other alkyl groups by reacting with an alkyl chlorosulfinate or chloroformate at an elevated temperature, the alkyl of the chlorosulfinate or chloroformate differing from the alkyl of the phosphate reacted upon. The extent of the replacement depends in part on the relative quantities of the two reactants which are present in the reaction mass. If desired, the alkyl phosphate employed as the starting material may be a mixed alkyl ester, in which case the product may contain a mixture of various alkyls. In the reaction described the use of equimolar quantities of the trialkyl phosphate and the alkyl chlorosulfinate or chloroformate gives primarily a product in which only one of the alkyls of the trialkyl phosphate is replaced. If the relative quantity of the alkyl phosphate is increased the replacement of more than one group of the trialkyl phosphate is minimized. On the other hand, the increase of the relative quantity of the alkyl chlorosulfinate or the alkyl chloroformate, favors the replacement of two, or in some cases, all three of the alkyl groups of the phosphate. Ordinarily the product which is obtained is a mixture of a phosphate in which only one alkyl has been replaced and a phosphate in which two of the alkyls have been replaced by the alkyl

2

of the other reactant. As triethyl phosphate is the most readily available of any of the trialkyl phosphates, the use of triethyl phosphate as the starting material in processes in accordance with my invention is particularly contemplated thereunder.

The temperature at which the reaction described is carried out may vary considerably but I have found that ordinarily the mass will be kept within the range of 120–200° C. over the major portion of the reaction. The temperature employed also is a factor in the time which will be used for the reaction to occur, although even at a high temperature cutting short the time will limit the replacement of alkyl groups in the alkyl phosphate used. In some cases a time of 2 hours will be sufficient, while in other cases, up to 4 hours or more will be desirable, while with the use of high temperatures or where the degree of the replacement of the alkyl groups is to be kept low, it may be that 1 hour would be sufficient.

The reaction may be carried out in a reaction vessel equipped with heating means and with means for agitating the mass. Also, provision should be made for the escape of the ethyl chloride and the sulfur dioxide or the carbon dioxide which is formed in the reaction. This is most conveniently done by providing the chamber wtih a reflux condenser whereby the gases referred to may escape whereas the higher boiling materials present in the mass will be returned to the reaction chamber.

The following examples illustrate my invention:

Example 1.—There was placed in a reaction vessel fitted with an agitator, a water-cooled condenser and a thermometer, 291 parts of triethyl phosphate (1.6 mol), and 250 parts (1.6 mol) of butyl chlorosulfinate. The mass was well agitated and the temperature was slowly raised. When the temperature reached 85° C. ethyl chloride and sulfur dioxide began to be evolved and was allowed to escape through the reflux condenser. The temperature was raised from 85° to 150° C. over a 2½-hour period and the mass was then maintained at 150° C. for ½ hour longer. The loss in weight as the result of this reaction was 164 parts or 80% of theoretical.

When the reaction mixture obtained was flash-distilled at a pressure of 1–2 mm., 27 parts of butyl chloride was collected in a Dry-Ice trap and 321 parts of mixed phosphates was obtained. 29 parts of the mass was lost through the pump during this distillation, most of which was sulfur dioxide and butylene. The 321 parts of mixed esters was redistilled through a spinning-band column at a reflux ratio of 49 to 1 to give the following fractions:

148 parts of triethyl phosphate
129 parts of diethyl butyl phosphate
43 parts of dibutyl ethyl phosphate

Phosphorus determinations showed 16.53%, 14.38% and 12.70% in the respective fractions as compared to theoretical phosphorus contents of 17%, 14.76% and 13%. This corresponds to 39% conversion to diethyl butyl phosphate and 11.6% conversion to dibutyl ethyl phosphate with a 62% utilization of the butyl group.

Example 2.—There was placed in a reaction vessel as described in the previous example a mixture of 214 parts (1 mol) of 2-ethyl hexyl chlorosulfinate and 365 parts (2 mol) of triethyl phosphate. This mixture was heated to 150° C. with good agitation over a 4-hour period. Ethyl chloride and sulfur dioxide began to be evolved through the reflux condenser at 90° C. Loss in weight was 92.5 parts or 72% of theoretical.

483 parts of the reaction mixture was then distilled at 2–3 mm. pressure through a short-path still to give the following fractions:

62 parts in a Dry-Ice trap of a mixture of 2-ethyl hexene and 2-ethyl hexyl chloride.
31 parts of 2-ethyl hexyl chloride at 30–40° C.
252 parts of triethyl phosphate at 56–60° C.
26 parts of a cut at 60–80° C., this cut being a mixture of triethyl phosphate and diethyl 2-ethyl hexyl phosphate.
83.5 parts taken at 80–100° C. essentially consisting of diethyl 2-ethyl hexyl phosphate.

The residue was 15.5 parts and the loss during distillation, most of which was SO_2, was 23 parts.

The reaction as described herein may take place using any alkyl group up to 10 carbon atoms. However, alkyl chlorosulfinates become less stable as their molecular weight increases so that lower yields are obtained with the higher alkyl compounds. By my invention, however, phosphates containing any groups from methyl up through ethyl, propyl and butyl to alkyls of 10 carbon atoms may be prepared, the conditions for any combination of alkyl groups being within the judgment of the individual operator as adapted to the compounds being prepared.

Example 3.—182 parts of triethyl phosphate (1 mol) and 124.5 parts (.912 mol) of butyl chloroformate were mixed together and heated with good agitation to 145° C. The temperature was then raised to 180° C. over a 4-hour period and the ethyl chloride and CO_2 as well as the HCl and butene formed were allowed to escape through a reflux condenser with which the reaction vessel was equipped. The reaction mass obtained was fractionated in a spinning-band column and there was obtained 46.1 parts of diethyl butyl phosphate, 20.3 parts of dibutyl ethyl phosphate, 111.1 parts of triethyl phosphate and a residue of 19.5 parts. The yield on the basis of the ethyl phosphate was 92% and on the basis of the butyl group utilized was 43%.

The reactions which occur in the various processes of my invention may be illustrated by the following equations:

$$(RO)_3P{=}O + R'O\overset{\overset{O}{\|}}{S}{-}Cl \longrightarrow RCl + SO_2 + (RO)_2\overset{\overset{O}{\|}}{P}{-}OR'$$

$$(RO)_3P{=}O + 2R'O\overset{\overset{O}{\|}}{S}{-}Cl \longrightarrow 2RCl + 2SO_2 + (R'O)_2\overset{\overset{O}{\|}}{P}{-}OR$$

$$(RO)_3P{=}O + R'O\overset{\overset{O}{\|}}{C}{-}Cl \longrightarrow RCl + CO_2 + (RO)_2\overset{\overset{O}{\|}}{P}{-}OR'$$

$$(RO)_3P{=}O + 2R'O\overset{\overset{O}{\|}}{C}{-}Cl \longrightarrow 2RCl + 2CO_2 + (R'O)_2\overset{\overset{O}{\|}}{P}{-}OR$$

In these equations R and R' may be any alkyls from 1 to 10 carbon atoms. As my invention is particularly adapted to the incorporation of different alkyl groups, it is preferable that the trialkyl phosphate used as the starting material be either triethyl or trimethyl phosphate and that the replacing alkyls be those of three or more carbon atoms. The products of my invention are useful for the preparation of various phosphorus containing insecticide compositions or may, in some cases, be useful for plasticizing purposes.

I claim:

1. A method for replacing, at least partially, the alkyl groups of a trialkyl phosphate the alkyl of which is of 1–10 carbon atoms which comprises reacting therewith at 120–200° C. a compound selected from the group of the alkyl chlorosulfinates and the alkyl chloroformates, the alkyl groups of which are of 1–10 carbon atoms and differ from those of the trialkyl phosphate, for a time sufficient to replace some of the alkyl groups of the trialkyl phosphate with alkyl groups from the other reactant used.

2. A method of replacing alkyl groups from a trialkyl phosphate which comprises reacting at 120–200° C. the trialkyl phosphate the alkyl of which is of 1–10 carbon atoms with an alkyl chlorosulfinate, having an alkyl of 1–10 carbon atoms which differs from that of the alkyl phosphate whereby a mixed alkyl phosphate is obtained.

3. A method of replacing alkyl groups from a trialkyl phosphate which comprises reacting at 120–200° C. the trialkyl phosphate the alkyl of which is of 1–10 carbon atoms with an alkyl chloroformate, having an alkyl of 1–10 carbon atoms which differs from that of the alkyl phosphate whereby a mixed alkyl phosphate is obtained.

4. A method of preparing a mixed alkyl phosphate which comprises reacting at 120–200° C. triethyl phosphate with an alkyl chlorosulfinate, the alkyls of which are of at least 3 and no more than 10 carbon atoms whereby some of the ethyl groups of the triethyl phosphate are replaced by higher alkyl groups.

5. A method of preparing a mixed alkyl phosphate which comprises reacting at 120–200° C. triethyl phosphate with an alkyl chloroformate, the alkyls of which are of at least 3 and no more than 10 carbon atoms whereby some of the ethyl groups of the triethyl phosphate are replaced by higher alkyl groups.

6. A method of preparing a mixed ethyl butyl phosphate which comprises reacting at 120–200° C. triethyl phosphate and butyl chlorosulfinate whereby some of the ethyl groups of the triethyl phosphate are replaced by butyl groups.

7. A method of preparing an ethyl, 2-ethyl hexyl phosphate which comprises reacting triethyl phosphate with 2-ethyl hexyl chlorosulfinate at 120–200° C., whereby some of the ethyl groups of the triethyl phosphate are replaced by 2-ethyl hexyl groups.

8. A method of preparing ethyl butyl phosphate which comprises reacting triethyl phosphate with butyl chloroformate at 120–200° C. whereby some of the ethyl groups of the triethyl phosphate are replaced with butyl groups.

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