This invention relates to a method for converting a phosphorous compound, e.g. phosphite or a phosphorous acid, to a phosphonate, particularly methane phosphonates, by reaction with an ester of a phosphoric acid, particularly selected from the methyl esters.

Methane phosphonic acid derivatives have been made by pyrolysis of dimethyl phosphate alone but not by reaction of the phosphate ester or of phosphoric acid with an ester of another oxy-acid, particularly such as a phosphoric acid.

For the present invention, it was found that the methane phosphonic acid derivatives can be obtained by reaction of phosphoric acid or methyl phosphites with methyl esters of phosphoric acid, and the yields of desired product are better than in the absence of the methyl phosphate esters.

The desired methane phosphonic acid derivatives are represented by the following general formula:

$$\text{R}_1\text{O-P}$$

wherein R1 and R2 stand for hydrogen, methyl, or a phosphorus-containing radical. Specific examples of these derivatives are:

- Methane phosphonic acid
- Mono methyl methane phosphonic acid
- Pyro methane phosphonic acid
- Trimeric methane phosphonic acid anhydride

**EXAMPLES**

The reagent phosphite or phosphorous compound was mixed in a Pyrex tube with about an equal volume of the methyl phosphate reactant. Another portion of the phosphite alone was also placed in a duplicate Pyrex tube. The liquid-containing tubes were heated side by side in a metal bath at temperatures mainly in the range of 100° to 300° C. A small amount of gas containing diethyl ether was evolved and was removed.

The reaction proceeded satisfactorily and the heating was stopped after a period of from 10 minutes to about 60 minutes. The trimethyl phosphate gave the quickest reaction for some extent of conversion at a given temperature.

The reaction product was cooled and weighed, then analyzed for P2O5 and P2O7, methane phosphoric acid, and total phosphorus content.

In general, the reaction products are clear, colorless liquids with densities above 1.0. On extended cooling at temperatures below 100° C., the products become solidified. On reheating the products are liquefied. The products are water-soluble.

The product obtained and described is useful as such, without further purification.

Other specific examples of the desired derivatives of the methane phosphonic acids shown are the dimethyl ester derivatives.

Improvements in yields of the desired methane phosphonic acid derivatives obtained by using the process of the present invention are shown in the following Table I.

**Table I**

<table>
<thead>
<tr>
<th>Reactant mixture</th>
<th>Mole percent P2O5 converted</th>
<th>Mole percent undesired P2O7 products</th>
<th>Desired phosphonate products</th>
<th>Yield percent of desired products</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. MMHP+H3PO4</td>
<td>99</td>
<td>6</td>
<td>94</td>
<td>96</td>
</tr>
<tr>
<td>B. MMHP+H3PO4+Me3PO4</td>
<td>95</td>
<td>6</td>
<td>91</td>
<td>95</td>
</tr>
<tr>
<td>C. Me3PO4+P2O7</td>
<td>95</td>
<td>0</td>
<td>100</td>
<td>95</td>
</tr>
<tr>
<td>D. H3PO4+Me3PO4</td>
<td>90</td>
<td>0</td>
<td>100</td>
<td>90</td>
</tr>
<tr>
<td>E. MMHP+H3PO4</td>
<td>95</td>
<td>6</td>
<td>99</td>
<td>95</td>
</tr>
<tr>
<td>F. MMHP+H3PO4+Me3PO4</td>
<td>92</td>
<td>9</td>
<td>93</td>
<td>92</td>
</tr>
<tr>
<td>G. H3PO4</td>
<td>90</td>
<td>0</td>
<td>100</td>
<td>90</td>
</tr>
<tr>
<td>H. H3PO4+MP</td>
<td>90</td>
<td>9</td>
<td>91</td>
<td>91</td>
</tr>
</tbody>
</table>

The summarized data in Table I shows in the duplicate experiments C and D that the presence of an equal amount of trimethyl phosphate did not affect the percentage of H3PO4 decomposed but changed the course of this decomposition from 100% undesired products to 97% desired products methane phosphonic acid derivatives.

In the pair of experiments G and H, mixed mono- and di-methyl phosphates caused H3PO4 to yield selectively 62% of the desired methane phosphonic acid derivatives instead of giving 100% conversion to undesired products.

The mixture of monomethyl phosphate and phosphorus acid referred to in the Table I as Sample A and Sample B were obtained by analysis of their aqueous solutions about 82 mole percent total phosphites including 52 mole percent monomethyl phosphate, 30% H3PO4 and 1% dimethyl phosphate. These mixtures were obtained at bottoms in the distillation of crude dimethyl phosphate (DMHP).

In the absence of the added methyl phosphites or similarly reacting esters, there is a low yield of only 20% of the desired products per pass or per fresh batch. In the duplicate experiment B, the added trimethyl phosphite raised the conversion to 90% from 37% and changed the yield to 82% of desired products per pass, which is a considerable advantage. Similarly, in the experiments E and F the mixed added methyl phosphites enhanced the yield of desired products although under
these conditions they did not change the total phosphite conversion level very much. It has been found that dimethyl hydrogen phosphite (DMHP) when pyrolyzed initially forms no appreciable amount of phosphates. As the pyrolysis reaction proceeds, substantial amounts of material which analyses in aqueous solutions as monomethyl phosphate (MMHP) and dimethyl phosphate and which contains these are converted into more undesired products, phosphates and phosphines. Accordingly, it is beneficial to add methyl phosphate esters at some stage of the pyrolysis for conversion of phosphites to the desired phosphonate derivatives.

In the examples given in the Table I, extraneous phosphate esters were added to the pyrolysis feeds to ascertain the specific effects of the phosphate esters. In an improved embodiment, the present invention contemplates the production of dimethyl phosphate along with dimethyl phosphate by judicious addition of POCl₃ to the PC₁₀ feed to methanol to form such a mixture.

Another embodiment of this invention involves the addition of trimethyl phosphate or similar ester to the reaction mixture in the pyrolysis of dimethyl hydrogen phosphate at the proper time for obtaining maximum yield. In the staged recirculating pyrolysis of DMHP this invention envisages the addition of the methyl ester to a point near the end of the pyrolysis. For example in an apparatus containing two circulating units the ester is added to the effluent before or during addition of the effluent to a final pyrolysis state.

The use of methyl esters such as trimethyl phosphate does not exclude the use of BF₃ or other such catalysts. In fact where trimethyl or dimethyl phosphate is added to DMHP in a pyrolysis reaction, BF₃ may also have been added. One attractive process involves the use of BF₃ to catalyze the desired reactions at the beginning and the addition of methyl phosphates to give better yields during the last half of the reaction when large amounts of unconverted phosphites such as monomethyl phosphate and H₃PO₄ are present.

In staged pyrolysis such as that above it is advantageous to use methyl phosphates in the higher temperature, second stage. BF₃ is especially beneficial at lower temperature early stages.

Study of the action of tri- or dimethyl phosphate on phosphoric acid indicates that ester interchange may occur. This concept does not limit the invention, however, and is not meant to indicate that mono- or dimethyl phosphate is essential to the production of methane phosphonic acid derivatives.

While trimethyl phosphate is a more desirable methylation agent, it costs more than di- or monomethyl phosphate. On the basis of equal methyl content it may be no more desirable. One view holds that the last methyl, i.e., the one visualized as held by the weakly acid POH, is the reactive one. On this basis the trimethyl phosphate has two methyls in reserve but the active methyl is the same as or similar in activity to that in mono-methyl phosphate. This concept is not to be construed as limiting the invention.

The temperature required for the above-discussed methylation ranges between an upper limit of about 350°C and a lower limit determined by that resulting from spontaneous reaction of the cold reagents. It is believed that 100°C to 275°C is a preferred operating range. The amounts of methylaing agents used is of course influenced by many considerations including the feed composition, catalyst, temperature and the economics of the particular reaction. Excess trimethyl phosphate of course would give the maximum yield and fastest reaction according to the present interpretation of the data.

Phosphates are desirable agents since present processes for phosphate pyrolysis include systems for handling these pyrolytic products. Borates are attractive because of the possibility that they might be regenerable with methyl alcohol to give volatile trimethyl borate.

In special cases other methyl esters might be more desirable.

It is envisioned that mixtures of methyl esters might be especially interesting. Methyl chloride in methyl phosphate or borate is suggested.

Products of this invention may be employed in preparing fuel, lubricating oil, and grease additives, detergents, fire retardants, insecticides, and plasticizers. The methane phosphonic acids undergo reaction with alcohols, esters, salts, bases, as well as with halogens and non-metallic halides.

In addition to the preceding ideas many others will now be obvious to those skilled in the art.

The invention described is claimed as follows:

1. Process for preparing a methane phosphonate which comprises reacting a phosphorous compound selected from the group consisting of phosphoric acid and methyl esters thereof with a methyl ester of a phosphoric acid.

2. Process for preparing a methane phosphonate by reacting a phosphorous acid and a methyl ester thereof with a methyl ester of a phosphoric acid.

3. Process for preparing a methane phosphonic acid and methyl esters thereof which comprises reacting a phosphite with a methyl ester of a phosphoric acid.

4. Process for preparing a methane phosphonic acid and a methyl ester thereof which comprises reacting a phosphorous acid with a methyl ester of a phosphoric acid.

5. Process for preparing a methane phosphonic acid and a methyl ester thereof which comprises heating a mixture containing phosphorous acid and methanol with a mixture containing mono- and dimethyl phosphate to temperatures in the range of 100°C to 350°C.

6. Process for preparing a methane phosphonic acid and methyl esters thereof which comprises heating a mixture containing phosphorous acid and mono-methyl phosphate with trimethyl phosphate to temperatures in the range of 100°C to 350°C.

No references cited.