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PREPARATION OF TRIALKENYL PHOSPHITES

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The present invention relates to the preparation of triallyl phosphite and trimethallyl phosphite.

It is an object of the present invention to prepare triallyl phosphite and trimethallyl phosphite from triaryl phosphites in a more economical fashion than has previously been possible.

An additional object is to prepare triallyl phosphite and trimethallyl phosphite from triphenyl phosphite in increased yields.

A further object is to prepare triallyl phosphite and trimethallyl phosphite from triphenyl phosphite with the elimination of by-product formation.

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 been proposed previously to react alkanols or alkenols with triaryl phosphites in substantially equivalent amounts in the presence of a small amount of an alkaline catalyst such as an alkali metal hydroxide or alcoholate. Such a procedure results in the formation of trialkyl phosphite in yields of 95% or above with alkanols of 8 or more carbon atoms. However, with lower alkanols and with alkenols such as allyl alcohol, for example, the yields of the desired product are considerably reduced and mixed alkyl aryl phosphites or alkenyl aryl phosphites are also formed. Thus, utilizing 3.1 mols of allyl alcohol, 1 mol of triphenyl phosphite and 0.04 mol of sodium, the product obtained included 65% triallyl phosphite and 20% diallyl phenyl phosphite.

It has also previously been proposed to react 3 mols of sodium alkoxide (from alkanols) with triphenyl phosphite to form trialkyl phosphites. When an attempt was made to extend such processes to the preparation of triallyl phosphite, it was found that there was obtained a substantial amount of the diallyl phenyl phosphite admixed with the desired triallyl phosphite. Trouble is encountered if an attempt is made to separate the triallyl phosphite from the diallyl phenyl phosphite.

It has now been found that it is possible to form triallyl phosphite or trimethallyl phosphite in yields of 75–80% and of a purity as high as 98.5% or higher, while completely eliminating the formation of the undesired diallyl phenyl phosphite or dimethallyl phenyl phosphite by reacting a large excess of the alkenol and sufficient alkali metal hydroxide to react with all the phenol formed in the reaction.

While preferably triphenyl phosphite is used as the starting triaryl phosphite, there can also be used other triaryl phosphites such as tri-p-cresyl phosphite, tri-o-cresyl phosphite, tri-m-cresyl phosphite, tri-2,4-xylenyl phosphite, tributylphenyl phosphite and trihaloaryl phosphites, such as tri-o-chlorophenyl phosphite, tri-o-bromophenyl phosphite, tri-p-chlorophenyl phosphite and tri-m-chlorophenyl phosphite.

As the alkenol, there is used allyl alcohol and methallyl alcohol.

As the alkali metal hydroxide, there is used sodium hydroxide or potassium hydroxide.

For each mol of triphenyl phosphite there should be used at least 4.5 mols of allyl alcohol or trimethallyl alcohol and preferably there are used 6 mols of the alcohol. Generally, there is no need to employ over 6 mols of the alcohol, which is a 100% excess, although there can be used more alcohol, e. g., as much as 9 mols or more. When less than 6 mols of alcohol are employed, the yields go down and the reaction slurry becomes thicker and more difficult to stir.

Enough of the sodium hydroxide should be employed to react with all the phenol formed. While an excess of sodium hydroxide over this amount can be employed, this is somewhat more costly.

The reaction is preferably carried out with stirring at a temperature not over 40° C. Room temperature has been found convenient. The reaction is normally complete in one half hour, although shorter times, e. g., 15 minutes, or longer times, e. g., 2 hours, can be employed.

The product obtained is drowned in water and the two layers separated. The sodium phenolate passes into the aqueous layer while the trialkenyl phosphite is in the organic layer and can be conveniently recovered therefrom by fractional distillation under reduced pressure.

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

Example 1

6 mols of allyl alcohol were mixed with one mol of triphenyl phosphite. Then 3 mols of powdered sodium hydroxide were gradually added with stirring until the addition was complete. The temperature of the mixture was kept under 40° C. throughout the reaction. At the end of one half hour, the mixture was drowned in water and two layers formed. The water layer was discarded and the organic layer was fractionally distilled. There was recovered triallyl phosphite in a yield of 80% based on the triphenyl phosphite starting material; the triallyl phosphite was 98.5% pure.

Example 2

Example 1 was repeated utilizing methallyl alcohol in place of the allyl alcohol. Trimethallyl phosphite of outstanding purity was obtained in excellent yields.

I claim:

1. A process of preparing a trialkenyl phosphite selected from the group consisting of triallyl phosphite and trimethallyl phosphite comprising transesterifying an aromatic phosphite selected from the group consisting of triaryl phosphites wherein the aryl group is selected from the group consisting of phenyl and lower alkyl substituted phenyl and trihalophenyl phosphites with at least 4.5 mols of an alkenol selected from the group consisting of allyl alcohol and methallyl alcohol for each mol of the aromatic phosphite in the presence of sufficient alkali metal hydroxide to neutralize the phenol formed in the reaction.

2. A process of preparing a trialkenyl phosphite selected from the group consisting of triallyl phosphite and trimethallyl phosphite comprising transesterifying triphenyl phosphite with at least 4.5 mols of an alkenol selected from the group consisting of allyl alcohol and methallyl alcohol for each mol of the triphenyl phosphite in the presence of sufficient alkali metal hydroxide to neutralize the phenol formed in the reaction.

3. A process according to claim 2 wherein the alkali metal hydroxide is sodium hydroxide.

4. A process according to claim 2 wherein the trialkenyl phosphite is triallyl phosphite and the alkenol is allyl alcohol.

5. A process according to claim 2 wherein the trialkenyl phosphite is trimethallyl phosphite and the alkenol is methallyl alcohol.

6. A process of preparing a trialkenyl phosphite selected from the group consisting of trialllyl phosphite and trimethallyl phosphite comprising transesterifying triphenyl phosphite with about 6 to 9 mols of an alkenol selected from the group consisting of allyl alcohol and methallyl alcohol for each mol of triphenyl phosphite in the presence of sufficient sodium hydroxide to neutralize the phenol formed in the reaction.

7. A process according to claim 6 wherein the trialkenyl phosphite is triallyl phosphite and the alkenol is allyl alcohol.

8. A process according to claim 7 wherein there are used 6 mols of allyl alcohol for each mol of triphenyl phosphite.

9. A process according to claim 6 wherein there are used 6 mols of alkenol for each mol of triphenyl phosphite.

10. A process according to claim 1 wherein the transesterification is carried out at a temperature between room temperature and 40° C.

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