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INHIBITION OF ISOMERIZATION OF ORGANIC COMPOUNDS

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This invention relates to inhibition of isomerization of organic compounds, and, more particularly, to a novel process for inhibiting thermal isomerization of terminal carbon-carbon double bonds.

The "shifting" of the carbon-carbon double bond or olefinic linkage of an olefinic compound to form the various isomers of the initial compound is, of course, well known. Thus, for example, a particular olefinic compound, such as octene, may in fact be present at least under certain conditions as an isomeric mixture of the terminal double bond compound, in this case 1-octene, and the various internal double bond isomers, i.e. 2-octene, 3-octene, etc.

Thermal isomerization, that is, isomerization of olefinic compounds induced by the application of heat, is particularly prevalent and it is the problem of undesirable thermal isomerization to which this invention relates.

It is, therefore, one object of this invention to prevent thermal isomerization of olefinic compounds.

Another object is to inhibit thermal isomerization by means of addition to the olefinic compound of certain phosphite inhibitors.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

As was indicated previously, this invention relates to a means for inhibiting thermal isomerization, thereby obviating the disadvantages resulting from the migration of the double bond or olefinic linkage from one carbon-carbon linkage to another carbon-carbon linkage in the molecule. It is well recognized that, in general, internal double bonds are more stable than the terminal isomers. Due to the tendency of double bonds normally to "shift" to the most thermodynamically stable position in the molecule when heat is applied, a terminal olefin, i.e., 1-octene, will tend to "shift" to one or more of the various internal olefins upon application of heat. This "shifting" to form one or more isomers of the initial terminal olefin is often undesirable, as will be appreciated by those skilled in the art. For example, where terminal olefins are used as intermediates in chemical reactions involving the addition of a substituent to the double bond, i.e., oxo synthesis, preparation of alkyl chlorides, aliphatic amines, etc., which reactions are often carried out at elevated temperatures, thermal isomerization will result in an isomeric mixture of the desired product. Moreover, olefins are often prepared by chemical processes involving the application of heat. Where synthesis of the terminal olefin is sought, thermal isomerization often results in obtaining an isomeric mixture of olefins in lieu of only the desired terminal olefin. This thermal isomerization or "shifting" to the more stable internal olefins may in fact result in a very poor yield of the terminal olefin.

I have now found that thermal isomerization may be precluded, or at least substantially inhibited, by the addition of an organic phosphite. The preferred organic phosphites useful in the practice of this invention may be represented by the formulae: $(RO)_3P$ and $(RO)_2POH$ wherein each R may be the same or different and may be alkyl, preferably lower alkyl, or aryl; and coordination compounds of such phosphites. As used herein, the expressions "alkyl" and "aryl" are intended to include substituted derivatives thereof.

As examples of alkyl phosphites within the above for-

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mula, mention may be made of trimethyl phosphite, triethyl phosphite, tribenzyl phosphite, etc. As examples of aromatic phosphites within the above formula, mention may be made of triphenyl phosphite, bis-(p-tolyl)-phenyl-phosphite, diphenyl phosphite, trinaphthyl phosphite, and nuclear substituted derivatives thereof, etc. As examples of coordination compounds of organic phosphites, mention may be made of bis-(triphenyl phosphite) chromium tetracarbonyl, etc. The particular proportions of the organic phosphite inhibitor added are not critical and may vary over a wide range. For optimum results, the ratio of organic phosphite inhibitor to olefinic compound may, for example, vary from 1:10 to 1:100. It should be apparent that lesser amounts of phosphite will inhibit isomerization at least to some extent, while greater amounts or excess phosphite may be utilized, if desired, although not necessary to produce the desired inhibition.

The organic phosphite may be utilized to inhibit thermal isomerization not only of alkenes, but of the various derivatives thereof, such as alcohols, esters, ethers, etc., containing at least one double bonded carbon to carbon linkage. As used herein, therefore, the term "olefinic compounds" is not restricted to alkenes, but includes organic compounds such as those mentioned above, containing one or more double bonded carbon to carbon linkages.

Where the olefinic compound is a liquid in which the organic phosphite is soluble, the phosphite may be dissolved directly therein to effect the desired inhibition. Otherwise, the olefinic compound and the phosphite inhibitor may be admixed in a suitable inert solvent, that is, a solvent which is inert to both the olefinic compound and the phosphite inhibitor. As examples of useful inert solvents, mention may be made of aromatic hydrocarbons such as benzene, xylene, toluene, and their derivatives, saturated aliphatic hydrocarbons such as pentanes, naphtha, kerosene, mineral oils, etc.; saturated alicyclic hydrocarbons such as cyclohexane, cyclopentane, etc.; lower alcohols such as methanol may also be used.

The following examples show by way of illustration and not by way of limitation the novel process of this invention.

Example 1

81 ml. of 1-octene were heated in a sealed container to 300° C. and a pressure of about 2,000 p.s.i. Analysis showed that most of the 1-octene was isomerized to internal olefins comprising predominantly 2-octene.

Example 2

A mixture of 79 ml. of 1-octene and 0.64 gram of bis-(triphenyl-phosphite)-chromium tetracarbonyl (as an example of a coordination compound) was heated to 285° C. in a sealed container under a pressure of about 1,800 p.s.i. Analysis showed 1-octene as the only remaining olefin.

The above examples illustrate how the presence of an organic phosphite inhibitor prevented isomeric "shifting" of the double bond to form one or more internal olefins. For purposes of illustrating this invention, an olefin having a plurality of available internal carbon atoms to which "shifting" may occur, to wit, 1-octene, was selected. Experiments with various homologues of 1-octene showed the same inhibiting power of an organic phosphite.

The following examples were carried out to ascertain the effect, if any, of additives to the reaction mixture. (For purposes of comparison only, the experiments with 1-octene are set forth.)

Example 3

40 ml. of 4-methyl-1-pentene, 40 ml. of benzene, 5 ml. of triethyl phosphite were heated at 200° C. for four hours in a sealed container under a pressure of about

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1,500 p.s.i. Analysis showed 4-methyl-1-pentene remained as the only olefin.

Example 4

40 ml. of 1-pentene, 40 ml. of methanol, and 1.64 grams of triphenyl phosphite were heated for 6 hours at 215° C. in a sealed container under a pressure of about 1,500 p.s.i. Analysis showed 1-pentene remained as the only olefin.

Example 5

40 ml. of 1-heptene was dissolved in 50 ml. of n-hexane and 3 grams of diphenyl phosphite were added. The mixture was heated to 200° C. for 5 hours in a sealed container under a pressure of about 1,500 p.s.i., and on analysis the only olefin remaining was found to be 1-heptene.

Since certain changes may be made in the above processes without departing from the scope of the invention herein involved, it is intended that all of the matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for inhibiting thermal isomerization of a monomeric terminal olefinic compound containing at least one non-equivalent internal carbon-to-carbon single bond, said compound being susceptible to isomerization by shifting of the terminal double bond to said internal position; which process comprises adding to said olefinic compound an organic phosphite selected from the group consisting of $(RO)_3P$, $(RO)_2POH$ and coordination compounds thereof, wherein each of the R groups is selected from the group consisting of monovalent alkyl and aryl hydrocarbon radicals.

2. The process as defined in claim 1 wherein said ole-

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finic compound is a liquid and said phosphite is dissolved therein.

3. The process as defined in claim 1 wherein said olefinic compound and said phosphite are dissolved in an inert solvent.

4. The process of claim 1 wherein the olefinic compound is 1-octene and the organic phosphite is triethyl phosphite.

5. The method of claim 3 wherein the inert solvent is benzene.

6. A composition of matter stabilized against thermal isomerization of a terminal olefinic bond, consisting essentially of a major portion of a monomeric terminal olefinic compound containing at least one non-equivalent internal carbon-to-carbon single bond, and a minor portion of an organic phosphite selected from the group consisting of $(RO)_3P$, $(RO)_2POH$ and coordination compounds thereof, wherein each of the R groups is selected from the group consisting of monovalent alkyl and aryl hydrocarbon radicals.

7. A stabilized composition of matter consisting essentially of the composition according to claim 6 dissolved in an inert solvent.

8. A composition of matter stabilized against thermal isomerization of a terminal olefinic bond, consisting essentially of a major portion of 1-octene and a minor portion of triethyl phosphite.

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