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[54] **PROCESS FOR THE ISOMERIZATION OF CIS-ISOMERIC HEXADIENOIC ACIDS**

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[56] **References Cited**

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[57] **ABSTRACT**

Process for the isomerization of cis-isomeric hexadienoic acids to sorbic acid in the presence of complex compounds of the platinum metals as catalysts.

8 Claims, No Drawings

PROCESS FOR THE ISOMERIZATION OF CIS-ISOMERIC HEXADIENOIC ACIDS

The present invention relates to the isomerization of cis-isomeric hexadienoic acids.

In the preparation of sorbic acid, which is essentially important as preservative for food, a mixture of cis-isomeric hexadienoic acids generally occurs as by-product, i.e. the cis-cis-, cis-trans- and/or trans-cis-hexadienoic acids. In the most important industrial manufacturing processes, such as the oxidation of sorbic aldehyde or the splitting of the polyester obtained from ketene and crotonic aldehyde, cis-isomeric acids are formed in amounts of up to 20%. These isomers have a lower melting point than sorbic acid and are obtained as an oily product. Since they are relatively sensitive to atmospheric oxygen, accelerate the oxidation and therefore can impair the stability of the sorbic acid, the latter must be carefully purified. The formation of these isomers involves, therefore, on the one hand, a loss of sorbic acid and, on the other, of materials, which are necessary for the elimination of the isomers. A technically applicable process for the isomerization of the cis-isomeric hexadieoic acids to sorbic acid is therefore of economic importance.

A process is already known wherein the cis-isomeric hexadienoic acids are treated with sulfur or such sulfur compounds from which free sulfur is obtained under the reaction conditions and/or hydrogen chloride at temperatures of from 20° to 300°C, preferably from 100° to 220°C. The applicability of this process is impaired by an unavoidable formation of volatile, unpleasantly smelling compounds, which contain sulfur and which contaminate the sorbic acid and by the known corrosion problems arising with the use of the hydrogen chloride.

It has now been found that these disadvantages can be avoided if certain complex compounds of platinum metals are used as isomerization catalysts.

The present invention relates to a process for isomerization of cis-isomeric hexadienoic acids to sorbic acid wherein the isomerization is carried out catalytically in the presence of complex compounds of the platinum metals in their various valence stages, preferably palladium in the elementary and bivalent stage. This finding is surprising in that the esters of the cis-isomeric hexadienoic acids cannot be isomerized with these complex compounds to the corresponding sorbic acid esters.

The free cis-isomeric hexadienoic acids can be isomerized, on the other hand, with these complex compounds in homogeneous and heterogeneous liquid phase and likewise in the gas phase.

As platinum metals are suitable the precious metals platinum, palladium, rhodium, iridium, ruthenium and osmium, which are closely related from the chemical point of view. For the process of the invention palladium is preferred for reasons of price and of catalytic effectiveness.

The precious metal complex used as catalyst contains preferably at least one neutral complex ligand containing an element of the groups V*b* and VI*b* of the Periodic System and having a free pair of electrons available as donator, preferably phosphorous. Neutral, complex forming ligands of this type are for example:monoalkyl- or monoaryl-, dialkyl-, trialkyl-amines, ethers, phosphines, arsines, stibines, mercaptans, sulfoxides, phosphites, arsenites, stibinites or pyridine. Further ligands may be: nitriles, keto-enolates or Schiff bases of keto-enolates, carboxylates, halides or metal salts, such as chlorides, sulfates, phosphates or acetates of potassium, sodium, lithium, zinc, cadmium or tin. The trialkyl- or triarylphosphine complexes of palladium in the elementary and bivalent stage are preferred, as for example tetrakis(triphenyl-phosphine)-palladium, (maleic anhydride)-bis-(triphenylphosphine)-palladium, bis(triphenyl-phosphine)-palladium chloride or other salts of bis(triphenyl-phosphine)-palladium, such as the acetate, acetonylacetate or hexadiene-2,4-oate-1.

The complex compounds used according to the invention can be added as such to the reaction mixture; they can however also be prepared in situ by adding the complex forming components, such as for example palladium(II)-acetate and triphenyl-phosphine to the reaction mixture at the same time or in separate stages. A further possibility is to apply the platinum metal on which the complex is based, for example palladium in metallic form or in the form of a compound, on an inert carrier and to add the complex forming ligands together with the mixture to be isomerized.

The reaction temperatures in question for the isomerization can differ in a wide range and are not critical for the process of the invention. In general, the process is carried out at a temperature of between 20° and 300°C, preferably between 50° and 250°C, but isomerization also takes place outside these temperature regions.

When carrying out the process of the invention in the liquid phase the product to be isomerized, which may contain, besides the cis-cis, cis-trans- and/or trans-cis-hexadienoic acids, sorbic acid and optionally inert solvents or diluents, is treated with the catalyst which is dissolved, suspended or supported on a carrier. The sorbic acid obtained is, separated expediently by crystallization from the reaction mixture optionally after separation from the catalyst. However, other processes of separation can also be used, for example extraction or absorption. The separated catalyst can also be used again as such or as solution in the mother liquor.

When working in the gas phase catalysts for example supported on a carrier, are used and the mixture to be isomerized is passed over the catalyst in the gaseous condition, optionally in the presence of an inert diluent, such as nitrogen or carbon dioxide. The isomerization is carried out preferably in diminished pressure of between 0.1 and 100 mm Hg on account of the high boiling point of the hexadienoic acids. After condensation the crystalline sorbic acid is separated in the usual way. Instead of the complex compound itself the component containing the platinum metal can also be supported alone on the carrier, for example palladium chloride, and the complex forming ligands can be added with the product to be isomerized regularly or periodically.

A further preferred method of technical importance is to pass the distillate, obtained during the thermal splitting of ketene-crotonic aldehyde polyester in the presence of an entrainer, over the supported catalyst containing the complex compounds in the gaseous condition before condensation.

The following examples illustrate the invention. The distribution of isomers before and after the reaction was ascertained by converting the hexadienoic acid into the methyl esters with gaschromatographic analy-

sis of the latter. The percentages are by weight unless otherwise stated.

EXAMPLE 1

100 Grams of a hexadienoic acid mixture, which consisted of 18.5% sorbic acid and 81.5% cis-isomers, were mixed with 2 g of palladium bis-acetyl-acetonate and 3.5 g of triphenyl phosphine and heated while stirring for 15 minutes at 100°C. 98% of the cis-isomers were converted into sorbic acid.

EXAMPLE 2

100 Grams of hexadienoic acid mixture of the composition specified in Example 1 were heated with 1.5 g of platinum-II-chloride and 3 g of triphenyl phosphine for 20 minutes at 100° to 110°C. Over 95% of the cis-isomers were converted into sorbic acid.

EXAMPLE 3

100 Grams of hexadienoic acid mixture of the composition specified in Example 1 were heated for 15 minutes at 100°C after adding 1.0 g of ruthenium-III-chloride hydrate and 2.5 g of triphenyl phosphine. 96% of the cis-isomers were converted into sorbic acid.

EXAMPLE 4

The process carried out in Example 1, however, instead of 2 g of palladium-bis-acetylacetonate 1.8 g of rhodium-triacetate were added to the reaction mixture. 90% of the cis-isomers present were converted into sorbic acid.

EXAMPLE 5

100 Grams of hexadienoic acid mixture of the composition specified in Example 1 were heated for 30 minutes at 100°C with 1.5 g of iridium acetate, the iridium content of which was 47.3%, and 2.0 g of triphenyl phosphine. 82% of the cis-isomers were converted into sorbic acid.

EXAMPLE 6

100 Grams of a solution of 11% sorbic acid and 32% cis-isomeric hexadienoic acids in triethyleneglycol diethylether were heated for 30 minutes at 100° to 105°C in the presence of 1.0 g of palladium acetate and 2.5 g of triphenyl phosphine. After this treatment the reaction mixture contained over 40% sorbic acid.

EXAMPLE 7

100 Grams of a solution of the composition specified in Example 6 were heated while stirring for 30 minutes at 100°C with 1.0 g of palladium acetate and 1.5 g of trimethyl arsine. After this treatment, the reaction mixture contained less than 1.5% of cis-isomeric hexadienoic acids.

EXAMPLE 8

The process was carried out as in Example 6, however, instead of 2.5 g of triphenyl phosphine, 3.5 g of triphenyl stibine were added to the reaction mixture. 86% of the isomeric hexadienoic acids were converted into sorbic acid.

EXAMPLE 9

100 Grams of a solution of the composition specified in Example 6 were heated while stirring for 30 minutes at 110°C with 1.0 g of palladium acetate and 0.7 g of thiourea. After this treatment less than 2.3% cis-isomeric hexadienoic acids remained in the reaction mixture.

EXAMPLE 10

100 Grams of the solution used in Example 6 with a cis-isomer portion of 32% were mixed with 1.8 g of triphenyl phosphine and 7.5 g of commercial palladium-carbon catalyst in powder form, with a palladium content of 5% by weight. The mixture was heated for 45 minutes at 80°C. 98% of the cis-isomers were converted into sorbic acid.

EXAMPLE 11

250 Milliliters of a catalyst, which contained 2% palladium metal on granular silicic acid carrier, were filled into a reaction tube with heated jacket. 500 Grams of a solution of 10% sorbic acid, 42% cis-isomeric hexadienoic acid and 1.5% triphenyl phosphine in toluene were passed upwardly over the catalyst at a temperature of 100° to 105°C. The product taken off at the upper end of the reaction tube contained less than 0.5% cis-isomers. After cooling to 10°C and separating the crystallized sorbic acid the mother liquor was used again for the preparation of further starting solution of the composition specified above and used again in the further course of the experiment. After 450 hours of operation the conversion was still unaltered.

EXAMPLE 12

1000 Grams of a vaporous mixture, which was obtained during the thermal splitting of a ketene-crotonic aldehyde polyester in the presence of alkaline catalysts according to the process of German Pat. No. 1.282.645, and which contained 15% sorbic acid, 5% cis-isomeric hexadienoic acids and 75% triethyleneglycol diethyl-ether, were passed per hour at 20 mm Hg and 150°C over 1 liter of a catalyst containing 8.5% palladium acetate and 12% triphenyl phosphine on a basic ion exchanger. After the condensation of the vapors the condensate contained only 1.5% cis-isomeric hexadienoic acids. The crystallized sorbic acid was separated and the mother liquor was used again in the thermal splitting of the polyester.

What is claimed is:

1. A process for the isomerization of cis-isomeric hexadienoic acids to sorbic acid, said process comprising isomerizing said hexadienoic acid catalytically at a temperature between 20° and 300°C in the presence of a complex compound of a platinum group metal selected from the group consisting of platinum, palladium, rhodium, iridium, ruthenium and osmium wherein the platinum group metal complex contains at least one neutral complex forming ligand with an element of groups V*b* and VI*b*, said ligands being monoalkyl-, dialkyl- or trialkyl-amines, triethyleneglycol diethylether, trialkylphosphines, tri-phenylphosphine, trimethylarsine, triphenylstibine, thiourea and pyridine.

2. Process as claimed in claim **1**, wherein a complex of palladium in the elementary or bivalent stage is used as catalyst.

3. Process as claimed in claim **1**, wherein the process is carried out in a solvent in homogeneous or heterogeneous liquid phase.

4. Process as claimed in claim **1**, wherein a distillate, which contains the cis-isomeric hexadienoic acids and which is obtained by thermal cleavage of ketenecro-

tonic aldehyde polyester in the presence of entrainers is used and the reaction is carried out in the gas phase before the condensation of the distillate.

5. Process as claimed in claim **1**, wherein the element of groups V*b* and VI*b* is phosphorus.

6. Process as claimed in claim **1**, wherein trialkyl- or triphenylphosphinic complexes of elementary and bivalent palladium are used.

7. The process as defined in claim **1**, wherein the complex is tetrakis(triphenyl-phosphine)-palladium; (maleic anhydride)-bis-(triphenylphosphine)-palladium; bis(triphenylphosphine)-palladium chloride or a salt of bis(triphenylphosphine)-palladium, wherein the salt is acetate, acetonylacetate or hexadiene-2,4-oate-1.

8. The process as claimed in claim **1** and wherein the ligand is a triphenyl phosphine.

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