

DESCRIPTION

METHOD FOR ISOMERIZATION OF ALLYL COMPOUND

5 TECHNICAL FIELD

The present invention relates to a method for isomerization of an allyl compound. More specifically, it relates to an isomerization method which is characterized in that by isomerization, from a 3,4-
10 diacetoxiallyl compound, a 1,4-diacetoxiallyl compound is formed as the corresponding compound.

BACKGROUND ART

Allyl compounds are important starting materials in
15 organic synthetic chemistry and are transformed into desired products by various reactions. Specifically, a diacetoxiallyl compound has a characteristic structure, whereby it is not only a compound which is transformable to various materials, but also an important intermediate
20 which is capable of producing diols by hydrolysis. Therefore, methods for producing various diacetoxiallyl compounds have been developed. For example, there has been a report of a method for producing diacetoxiallyl compound by diacetoxylation of butadiene by using a
25 rhodium solid catalyst (Patent Document 1). Most of the time, the diacetoxylation of a conjugated diene for the production of a diacetoxiallyl compound, proceeds in good

yield in the presence of a solid catalyst, but the current situation is that the position of an acetoxyl group to be introduced cannot be completely controlled. Specifically, in a reaction for producing 1,4-diacetoxy-2-butene which is a raw material for 1,4-butanediol, 3,4-diacetoxy-1-butene which is not transformable into 1,4-butanediol, is formed as a by-product. Therefore, in the production process of 1,4-butanediol, the cost of butadiene as a raw material has been pushed up.

10 Therefore, a method has been developed to isomerize such a by-product 3,4-diacetoxyallyl compound to form 1,4-diacetoxyallyl compound such as 1,4-diacetoxy-2-butene by isomerizing. For example, an isomerization reaction of 3,4-diacetoxy-1-butene to 1,4-diacetoxy-2-butene by
15 using a palladium complex catalyst having a phosphite ligand, is reported (Patent Document 2). Further, there has been a report that a more active isomerization catalyst is obtained by further adding a phosphonium compound in addition to the palladium complex catalyst
20 having a phosphite ligand (Patent Document 3). However, in such methods for isomerization of diacetoxyallyl compounds, catalysts become substantially deteriorated, whereby it was required to use a large amount of catalysts.

25 Such catalyst deterioration is considered to be caused by a catalyst deteriorating component contained in the diacetoxyallyl compound, and a method has been

reported to remove the catalyst deteriorating component by using a solid base (Patent Document 4). However, in such a method, the solid base adsorbs several acidic components in addition to the catalyst deteriorating component, and a large amount of the solid base is required. Therefore, a method has been desired which is industrially advantageous and is capable of efficiently removing or making harmless the catalyst deteriorating component.

10 Patent Document 1: JP-A-11-71327
 Patent Document 2: JP-A-2002-105025
 Patent Document 3: JP-A-2004-115506
 Patent Document 4: JP-A-2006-282564

15 DISCLOSURE OF THE INVENTION

 OBJECT TO BE ACCOMPLISHED BY THE INVENTION

 The object of the present invention is to provide, as a method for isomerization of an allyl compound by using a catalyst, an industrially advantageous method for isomerization of an allyl compound which suppresses catalyst deterioration and is capable of obtaining an isomer in good yield by using a small amount of a catalyst.

25 MEANS TO ACCOMPLISH THE OBJECT

 The present inventors have conducted extensive studies to achieve the above object, and as a result,

they have found that a component which substantially accelerates the deterioration of an isomerization catalyst contained in a liquid containing a diacetoxyallyl compound, can be removed by a phosphorus compound. Thus, the present invention has been accomplished. That is, the present invention provides the following (1) to (13).

- (1) An isomerization method comprising contacting a liquid containing an allyl compound as a raw material, with a phosphorus compound, and then, isomerizing the above allyl compound in the presence of a catalyst.
- (2) The isomerization method according to the above (1), wherein the above phosphorus compound is an organic phosphorus compound.
- (3) The isomerization method according to the above (2), wherein the above organic phosphorus compound is an organic phosphine.
- (4) The isomerization method according to the above (3), wherein the above organic phosphine has at least two aryl groups.
- (5) The isomerization method according to the above (3) or (4), wherein the above organic phosphine is triphenyl phosphine.
- (6) The isomerization method according to any one of the above (1) to (5), wherein the amount of the phosphorus compound which is contacted with the above allyl compound-containing liquid, is in a range of from 0.0001

to 10 weight%, based on the allyl compound.

(7) The isomerization method according to any one of the above (1) to (6), wherein the above allyl compound-containing liquid and the phosphorus compound are
5 contacted to each other at temperature of at least 60°C.

(8) The isomerization method according to any one of the above (1) to (7), which further includes a step of obtaining the above allyl compound-containing liquid by diacetoxylation of a conjugated diene.

10 (9) The isomerization method according to any one of the above (1) to (8), wherein the above catalyst is a liquid phase homogeneous palladium catalyst, which contains a phosphorus ligand having at least one P-O bond.

(10) The isomerization method according to the above (9),
15 wherein the above phosphorus ligand having a P-O bond, is a bidentate phosphite.

(11) The isomerization method according to the above (9), wherein the above phosphorus ligand having a P-O bond, is a bidentate phosphoramidite.

20 (12) The isomerization method according to any one of the above (1) to (11), wherein the above allyl compound is a 3,4-diacetoxyallyl compound, which forms, by isomerization, a 1,4-diacetoxyallyl compound as a compound corresponding to the above allyl compound.

25 (13) A process for producing an allyl compound, which comprises forming from an allyl compound the corresponding isomerized allyl compound by using the

isomerization method as defined in any one of the above (1) to (12).

EFFECT OF THE INVENTION

5 According to the present invention, in isomerization of a diacetoxiallyl compound by using a catalyst, it is possible to obtain an isomer in good yield by using a small amount of a catalyst.

10 BEST MODE FOR CARRYING OUT THE INVENTION

Now, the present invention will be described in further detail. The following description is directed to typical embodiments of the present invention, and the present invention is by no means restricted thereto.

15 Further, the allyl compound in the present invention is a compound having an allyl group and a compound to be formed by isomerization from the compound having an allyl group by using a catalyst. It is not particularly limited and includes all allyl compounds having a leaving
20 group such as an acetoxy group, halogen or a carboxylic acid at a position of the allyl group in such compounds. For example, in the present invention, the compound to be obtained by isomerization of a 3,4-diacetoxiallyl compound is a 1,4-diacetoxiallyl compound.

25 Further, the isomerization method of the present invention includes a method wherein a compound formed by isomerization of the compound having an allyl compound is

transformed into a compound having an allyl group.

The following embodiments of the present invention will be described with reference to an example of a case wherein by isomerization of a 3,4-diacetoxyallyl compound which is an allyl compound, a 1,4-diacetoxyallyl compound
5 which is the corresponding allyl compound, is formed.

"The method for isomerizing a 3,4-diacetoxyallyl compound to a 1,4-diacetoxyallyl compound" of the present invention, is a method for isomerizing a 3,4-
10 diacetoxyallyl compound as a raw material to a 1,4-diacetoxyallyl compound in the presence of a catalyst, which comprises contacting a liquid containing a 3,4-diacetoxyallyl compound as a raw material (hereinafter referred to as a 3,4-diacetoxyallyl compound-contained
15 liquid), with a phosphorus compound, and then, isomerizing the 3,4-diacetoxyallyl compound as a raw material in the presence of a catalyst.

By contacting a phosphorus compound with the 3,4-diacetoxyallyl compound-contained liquid, it is possible
20 to remove a component which substantially accelerates deterioration of the isomerization catalyst, by the phosphorus compound. As compared with a solid base, with a phosphorus compound, it is easy to change its amount to be added during the operation of the process, whereby by
25 observing the amount of the 1,4-diacetoxyallyl compound to be formed by isomerization, it is possible to suppress the catalyst deterioration with the minimum amount.

Further, unlike a solid base, it is not necessary to fill the prescribed amount before starting the process operation, whereby the amount to be used will be less.

"The method for isomerizing a 3,4-diacetoxyallyl compound to a 1,4-diacetoxyallyl compound by a catalyst" may, for example, be "a method for obtaining a 1,4-diacetoxyallyl compound by contacting a 3,4-diacetoxyallyl compound with a catalyst, for isomerization to a 1,4-diacetoxyallyl compound", "a method for increasing the concentration of a 1,4-diacetoxyallyl compound by contacting a mixture of a 3,4-diacetoxyallyl compound and a 1,4-diacetoxyallyl compound with a catalyst to isomerize the 3,4-diacetoxyallyl compound in the mixture to a 1,4-diacetoxyallyl compound" or "a method for increasing the concentration of a 3,4-diacetoxyallyl compound by contacting a mixture of a 3,4-diacetoxyallyl compound and a 1,4-diacetoxyallyl compound with a catalyst to isomerize the 1,4-diacetoxyallyl compound in the mixture to a 3,4-diacetoxyallyl compound."

In the present invention, the 3,4-diacetoxyallyl compound (including "the mixture of a 3,4-diacetoxyallyl compound and a 1,4-diacetoxyallyl compound") is not particularly limited, and it can be produced by e.g. diacetoxylation of a conjugated diene in the presence of a catalyst.

It is possible to carry out the diacetoxylation of a

conjugated diene, which produces a diacetoxiallyl compound, by various methods. In the most common method, butadiene, acetic acid and oxygen are reacted in the presence of a palladium type catalyst, to obtain
5 diacetoxiallyl compounds such as 1,4-diacetoxy-2-butene and 3,4-diacetoxy-1-butene. Further, hydrolysates of such diacetoxiallyl compounds are additionally formed such as 1-hydroxy-4-acetoxy-2-butene, 3-hydroxy-4-acetoxy-1-butene and 4-hydroxy-3-acetoxy-1-butene.

10 The conjugated diene which can be used in the present invention may, for example, be butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene, 1,3-cyclopentadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, 1,3-pentadiene, 1,3-hexadiene or 2,4-
15 hexadiene. It is preferably butadiene, isoprene, 1,3-cyclohexadiene or 1,3-cyclopentadiene, particularly preferably butadiene or isoprene. The reason for such preference is that a conjugated diene such as butadiene or isoprene having a small number of carbon atoms shows
20 the highest reactivity.

As a catalyst to be used for the diacetoxylation of a conjugated diene, it is possible to use any catalyst so long as it has an ability to transform the conjugated diene into a diacetoxiallyl compound. It is preferably a
25 solid catalyst containing a transition metal of Group 8 to 10, particularly preferably a palladium solid catalyst. The palladium solid catalyst is made of

palladium metal or its salt. As a promoter, it is preferred to use metal such as bismuth, selenium, antimony, tellurium or copper, or its salt, particularly preferably tellurium. The reason why a combination of
5 palladium and tellurium is preferred is that the reactivity of the catalyst is high, and the selectivity for a diacetoxyallyl compound to be obtained is high. Therefore, the catalyst is preferably a catalyst containing palladium and tellurium as active components.
10 The palladium solid catalyst is not particularly limited, but it is used preferably as supported on a carrier such as silica, alumina, titania, zirconia, active carbon or graphite. Silica is particularly preferred since it is excellent in strength. From the viewpoint of the
15 physical properties, the carrier is preferably porous, and specifically, it is preferably a porous carrier having an average pore diameter of from 1 to 100 nm, more preferably a porous carrier having an average pore diameter of from 5 to 80 nm. In the case of a catalyst
20 supported on a carrier, the proportion of the catalyst metal is usually selected from a range of from 0.1 to 20 wt%, preferably from 1 to 10 wt%, based on the entire catalyst. Further, the proportion of other promoter metals is selected from a range of from 0.01 to 30 wt%,
25 more preferably from 0.1 to 10 wt%, based on the entire catalyst. If such values are too small, the cost competing ability will decrease by the decrease of the

catalyst activity, and if such values are too large, the competing ability will decrease by the substantial increase of the catalyst cost.

The above diacetoxylation is preferably carried out
5 in air, oxygen-enriched air, air or oxygen diluted with
an inert gas such as nitrogen, or in the atmosphere of
oxygen. The concentration of oxygen may be in a range of
from 1 to 100 vol%, more preferably from 2 to 50 vol%,
particularly preferably from 3 to 40 vol%. The higher
10 the concentration of oxygen, the higher the reaction
rate, whereby it is possible to efficiently obtain the
product. On the other hand, as the concentration of
oxygen becomes low, there will be less risk of the
process such as explosion or fire.

15 The diacetoxylation may be carried out in either a
vapor phase or a liquid phase. The reaction temperature
is in a range of from 0 to 300°C, preferably from 10 to
250°C, more preferably from 30 to 200°C. The higher the
reaction temperature, the higher the reaction rate,
20 whereby it is possible to efficiently obtain the product.
On the other hand, as the reaction temperature becomes
low, there will be less risk of the process such as
explosion or fire. The reaction pressure is preferably
in a range of from atmospheric pressure to 50 MPa, more
25 preferably from atmospheric pressure to 30 MPa,
particularly preferably from 1 to 20 MPa.

When the diacetoxylation is carried out in a liquid

phase, a solvent to be used for the reaction is not particularly limited as long as it dissolves the reaction raw material. It is preferably water, a conjugated diene as the reaction raw material itself, such as butadiene or
5 carboxylic acid such as acetic acid, or a diacetoxiallyl compound as the product itself. Further, as the solvent, it is possible to use a hydrocarbon such as hexane, heptane or octane; an ether such as tetrahydrofuran, diethyl ether or triglyme; an ester such as butyl
10 butyrate; a ketone such as acetone or methyl isobutyl ketone; or an alcohol such as 1,4-butanediol.

The weight ratio of the conjugated diene as a raw material to the catalyst is preferably in a range of from 1 to 100,000,000, more preferably from 10 to 50,000,000,
15 particularly preferably from 100 to 20,000,000. The smaller the weight ratio, the higher the reaction rate, whereby the reaction tends to proceed in a short period of time. Further, the larger the weight ratio, the less the catalyst cost.

20 Further, in the present invention, "the 3,4-diacetoxiallyl compound-containing liquid" is not particularly limited as long as it is a liquid containing a 3,4-diacetoxiallyl compound or a mixture of 3,4-diacetoxiallyl compound and a 1,4-diacetoxiallyl
25 compound. For example, "the 3,4-diacetoxiallyl compound-containing liquid" is preferably (1) the reaction product stream itself obtained from a step of the diacetoxylation

of a conjugated diene by the above catalyst before contacting the 3,4-diacetoxyallyl compound-containing liquid with a phosphorus compound, (2) one having removed from the reaction product stream, by e.g. distillation, a part or the entire amount of compounds having lower boiling points than a diacetoxyallyl compound, formed as by-products (hereinafter the compounds having lower boiling points than a diacetoxyallyl compound will be referred to as low boiling point compounds), (3) one having removed from the reaction product stream, by e.g. distillation, a part or the entire amount of compounds having higher boiling points than the 3,4-diacetoxyallyl compound, formed as by-products (hereinafter the compounds having higher boiling points than the 3,4-diacetoxyallyl compound will be referred to as high boiling point compounds), or (4) one having removed from the reaction product stream, by e.g. distillation, parts or the entire amounts of low boiling point compounds and high boiling point compounds formed as by-products.

Among them, "the 3,4-diacetoxyallyl compound-containing liquid" is particularly preferably (1) the reaction product stream itself obtained by the diacetoxylation of the conjugated diene by a catalyst. When "the 3,4-diacetoxyallyl compound-containing liquid" is one derived from the reaction product stream itself obtained by the diacetoxylation of the conjugated diene by the above catalyst, the corresponding 1,4-diacetoxyallyl compound

is present in the liquid. Further, "the 3,4-diacetoxyallyl compound-containing liquid" may contain a hydrolysate of the 3,4-diacetoxyallyl compound such as a 3,4-hydroxyacetoxyallyl compound and/or a 3,4-dihydroxyallyl compound. Further, it may contain a hydrolysate of the 1,4-diacetoxyallyl compound such as a 1,4-hydroxyacetoxyallyl compound and/or a 1,4-dihydroxyallyl compound.

"The 3,4-diacetoxyallyl compound-containing liquid" used in the present invention, may be obtained in such a manner that a liquid containing a 3,4-diacetoxyallyl compound, and a 1,4-diacetoxyallyl compound, low boiling point compounds and high boiling point compounds, is introduced into a distillation column; the liquid containing high boiling point compounds and the 1,4-diacetoxyallyl compound is withdrawn from the bottom of the column; and the 3,4-diacetoxyallyl compound-containing liquid is obtained from the upper portion of the column by distillation. At that time, it is possible to withdraw the 3,4-diacetoxyallyl compound-containing liquid from the top of the column together with low boiling point compounds. Further, the 3,4-diacetoxyallyl compound-containing liquid may be withdrawn from a side-portion, and the low boiling point compounds may be distilled from the top of the column. In such a case, although the most amount of the high boiling point compounds is withdrawn from the bottom of the column, a

small amount of the high boiling point compounds is withdrawn from the top of the column or from the side-portion together with the 3,4-diacetoxyallyl compound-containing liquid.

5 Further, the pressure of the distillation column may optionally be set, but from the viewpoint of an energy cost required for a reboiler of the distillation column, the pressure at the top of the column is preferably set to be from 1 to 760 mmHg, in order to decrease the
10 temperature at the bottom of the column. Further, the pressure at the top of the column is more preferably from 5 to 200 mmHg, particularly preferably from 10 to 100 mmHg. If the pressure at the top of the column is too low, in order to maintain the pressure, a high cost will
15 be needed, and the distillation column itself will have to be large, whereby an installation cost for the process will increase. Further, if the pressure at the top of the column is too high, the temperature at the bottom of the distillation column will be high, whereby a steam
20 cost will increase. The temperature at the top of the column is usually from 0 to 200°C, preferably from 20 to 160°C, more preferably from 40 to 140°C. If the temperature at the top of the column is too low, a specific device such as a cooler will be needed, which
25 adds to the cost. Further, if the temperature is too high, the temperature at the bottom of the column will also be high, whereby the steam cost will increase. The

reflux ratio may be from 1 to 100, preferably from 1 to 10. If the reflux ratio is too small, separation ability tends to be deteriorated, and if the reflux ratio is too large, the amount of heat needed tends to increase, thus
5 leading to an increase of the cost. With respect to the amount of the distillation from the top of the column, it is desired to distill the total amount of the 3,4-diacetoxyallyl compound and the low boiling point compounds from the liquid introduced into the
10 distillation column, which contains the 3,4-diacetoxyallyl compound, and the 1,4-diacetoxyallyl compound, the low boiling point compounds and the high boiling point compounds.

Further, when the 3,4-diacetoxyallyl compound-
15 containing liquid is to be withdrawn from the side-portion, and the low boiling point compounds are to be distilled from the top of the column, it is preferred to withdraw the content of the 3,4-diacetoxyallyl compound in the feed liquid from the side-portion, and distill the
20 low boiling point compounds in the feed liquid from the top of the column.

In a case where the liquid containing the high boiling point compounds and the 1,4-diacetoxyallyl compound, is withdrawn from the bottom of the
25 distillation column, and the 3,4-diacetoxyallyl compound containing the low boiling point compounds is distilled from the top of the column, the balance of the substances

in the distillation column is such that the amount of the distillate from the top of the column per unit time is from 1 to 50, preferably from 5 to 30, based on the amount by weight of the feed liquid per unit time being 100. At that time, the amount withdrawn per unit time of the liquid containing the high boiling point compounds and the 1,4-diacetoxyallyl compound from the bottom of the column, is preferably from 50 to 99, more preferably from 70 to 95. Further, in a case where the liquid containing the high boiling point compounds and the 1,4-diacetoxyallyl compound, is withdrawn from the bottom of the distillation column, the low boiling point compounds are distilled from the top of the column, and the 3,4-diacetoxyallyl compound-containing liquid is withdrawn from the side-portion, the amount of the distillate from the top of the column per unit time is from 0.1 to 30, preferably from 1 to 20, based on the amount by weight of the feed liquid per unit time being 100. Further, the amount of the 3,4-diacetoxyallyl compound-containing liquid withdrawn from the side-portion is from 0.9 to 50, more preferably from 2 to 30. Further, the amount withdrawn per unit time of the liquid containing the high boiling point compounds and the 1,4-diacetoxyallyl compound from the bottom of the column is preferably from 20 to 99, more preferably from 50 to 97.

It is possible to supply the above 3,4-diacetoxyallyl compound-containing liquid which contains

the low boiling point compounds obtained from the top of the column, for an isomerization reaction, after removing the low boiling point compounds by distillation. In such a case, in a separation distillation column, the low
5 boiling point compounds are distilled from the top of the column, and the 3,4-diacetoxyallyl compound-containing liquid may be withdrawn from the bottom of the column including the side-portion.

Further, the pressure of the distillation column may
10 optionally be set, but from the viewpoint of an energy cost required for a reboiler of the distillation column, the pressure at the top of the column is preferably from 1 to 760 mmHg in order to decrease the temperature at the bottom of the column. Further, the pressure at the top
15 of the column is more preferably from 5 to 400 mmHg, particularly preferably from 10 to 200 mmHg. If the pressure at the top of the column is too low, in order to maintain the pressure, a high cost will be needed, and the distillation column itself will become large, whereby
20 an installation cost for the process will increase. Further, if the pressure at the top of the column is too high, the temperature at the bottom of the distillation column will be high, whereby a steam cost will increase. The temperature at the top of the column is usually from
25 0 to 200°C, preferably from 20 to 160°C, more preferably from 40 to 140°C. If the temperature at the top of the column is too low, a specific device such as a cooler

will be needed, which adds to the cost. Further, if the temperature is too high, the steam cost will increase, since the temperature will be higher than the temperature at the bottom of the column. A reflux ratio is

5 sufficient from 1 to 100, preferably from 1 to 10. If the reflux ratio is too small, separation ability tends to be deteriorated, and if the reflux ratio is too large, the amount of heat needed tends to increase and will become a cause of the cost deterioration.

10 With respect to the amount of the distillation from the top of the column, it is desired to distill the total amount of the low boiling point compounds from the liquid introduced into the distillation column, which contains the 3,4-diacetoxyallyl compound and the low boiling point
15 compounds. In a case where the 3,4-diacetoxyallyl compound-containing liquid is withdrawn from the bottom of the column including the side-portion of the distillation column, and the low boiling point compounds are distilled from the top of the column, the balance of
20 the substances in the distillation column is such that the amount of the distillate from the top of the column per unit time is from 1 to 50, preferably from 5 to 45, based on the amount by weight of the feed liquid per unit time being 100. At that time, the amount withdrawn per
25 unit time of the 3,4-diacetoxyallyl compound-containing liquid from the bottom of the column including the side-portion, is preferably from 50 to 99, more preferably

from 55 to 95.

The present invention is characterized in that the 3,4-diacetoxyallyl compound-containing liquid is contacted with a phosphorus compound. However, when the reaction product stream obtained in a step of diacetoxylation of a conjugated diene by a catalyst, is designated as "the 3,4-diacetoxyallyl compound-containing liquid", the reaction product stream may be contacted with a phosphine before distillation separation; or after the reaction product stream obtained by an acetoxylation reaction of the conjugated diene, is subjected to distillation separation, the 3,4-diacetoxyallyl compound-containing liquid distilled from the top of the column may be contacted with a phosphine or the 3,4-diacetoxyallyl compound-containing liquid distilled from the side-portion may be contacted with a phosphine. It is preferred to have the phosphorus compound contacted with the liquid distilled from the top of the column or the liquid withdrawn from the side-portion, since it is possible to exhibit an effect with a small amount of the liquid to be contacted and a small amount of the phosphorus compound.

The type of the distillation column may, for example, be a packed column or a plate column, and it is preferably a fractional column. To separate the 3,4-diacetoxyallyl compound-containing liquid from the 1,4-diacetoxyallyl compound-containing liquid, the number of

theoretical plates for the distillation column is preferably at least 3 plates, particularly preferably from 10 to 50 plates. The distillation column having more than 50 plates, is not preferred from the viewpoint
5 of economical efficiency for installation of the distillation column, difficulty of the operation and safety management. Further, if the number of the plates is too small, separation will be difficult.

The 3,4-diacetoxyallyl compound to be used for the
10 isomerization reaction of the present invention, is specifically preferably 3,4-diacetoxy-1-butene, 3,4-diacetoxy-2-methyl-1-butene, 3,4-diacetoxy-3-methyl-1-butene, 3,4-diacetoxy-2,3-dimethyl-1-butene, 3,4-diacetoxy-1-cyclohexene, 3,4-diacetoxy-1-cyclopentene,
15 3,4-diacetoxy-1-cycloheptene or 3,4-diacetoxy-1-cyclooctene, more preferably 3,4-diacetoxy-1-butene, 3,4-diacetoxy-2-methyl-1-butene, 3,4-diacetoxy-3-methyl-1-butene, 3,4-diacetoxy-1-cyclohexene or 3,4-diacetoxy-1-cyclopentene, particularly preferably 3,4-diacetoxy-1-
20 butene which is transformable into 1,4-diacetoxy-2-butene as an intermediate of 1,4-butanediol.

Further, the isomerization of the present invention is applicable to an isomerization reaction of 3-hydroxy-4-acetoxy-1-butene, 4-hydroxy-3-acetoxy-1-butene, etc.,
25 which are hydrolysates of 3,4-diacetoxy-1-butene.

Further, in the present invention, the 1,4-diacetoxyallyl compound obtained by isomerization of the

3,4-diacetoxyallyl compound, is the isomer corresponding to the 3,4-diacetoxyallyl compound before isomerization. The 1,4-diacetoxyallyl compound as an isomer is specifically preferably 1,4-diacetoxy-2-butene, 1,4-diacetoxy-2-methyl-2-butene, 1,4-diacetoxy-2,3-dimethyl-2-butene, 1,4-diacetoxy-2-cyclohexene, 1,4-diacetoxy-2-cyclopentene, 1,4-diacetoxy-2-cycloheptene or 1,4-diacetoxy-2-cyclooctene, more preferably 1,4-diacetoxy-1-butene, 1,4-diacetoxy-2-methyl-1-butene, 1,4-diacetoxy-3-methyl-1-butene, 1,4-diacetoxy-1-cyclohexene or 1,4-diacetoxy-1-cyclopentene, particularly preferably 1,4-diacetoxy-1-butene which is an intermediate of 1,4-butanediol.

In the present invention, it is possible to use various solvents when the isomerization reaction of the 3,4-diacetoxyallyl compound is carried out. The solvents are not particularly limited, and specifically, it is possible to use an organic solvent such as a carboxylic acid such as formic acid, acetic acid, propionic acid or butanoic acid; an alcohol such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol or octanol; an ether such as diethyl ether, tetrahydrofuran, dioxane or triglyme dimethyl ether; an aromatic hydrocarbon such as benzene, toluene or xylene; or a hydrocarbon solvent such as hexane, heptane, octane, nonane, decane, dodecane, cyclohexane, cycloheptane or cyclooctane. Preferred is a carboxylic acid such as

formic acid, acetic acid, propionic acid or butanoic acid, and particularly preferred is acetic acid which improves the rate of isomerization of an acetoxy group.

The reason why acetic acid is preferred as the solvent is
5 that in the reaction liquid, the concentration of the acetoxy group i.e. the concentration of acetic acid which contributes for improving the isomerization rate, will be high.

The amount by wt% of the solvent to be added is,
10 preferably from 0 to 10,000 wt%, more preferably from 0.05 to 500 wt%, particularly preferably from 1 to 200 wt%, based on the diacetoxiallyl compound. If the amount of the solvent to be added, is small, the volume of a reactor will be small. If the amount to be added is
15 large, the rate of the catalyst deterioration will tend to be low.

In the present invention, the catalyst to be used for isomerization of the 3,4-diacetoxiallyl compound, is not particularly limited as long as it has the ability to
20 isomerize the 3,4-diacetoxiallyl compound to the 1,4-diacetoxiallyl compound. It is a liquid phase homogeneous complex catalyst, preferably a homogeneous complex catalyst of a transition metal of Group 8 to 10, particularly preferably a liquid phase homogeneous
25 palladium complex catalyst which shows a particularly high activity to an acetoxy isomerization rate.

The liquid phase homogeneous complex catalyst may be

prepared from various transition metals, and it may, specifically, be an acetate, an acetylacetonate compound, a chloride, a bromide, an iodide, a sulfate, a nitrate, an organic salt, an inorganic salt, an olefin ligand compound, a carbon monoxide ligand compound, a phosphine
5 ligand compound or a phosphite ligand compound.

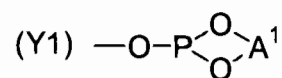
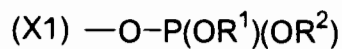
The liquid phase homogeneous complex catalyst is preferably palladium metal, palladium acetate, palladium chloride, dichlorocyclooctadiene palladium,
10 tetrakis(triphenyl phosphine) palladium, bis(dibenzylidene acetone)palladium, palladium trifluoroacetate, palladium acetylacetonate, nickel acetate, dicyclooctadiene nickel, platinum acetate or dicyclooctadiene platinum, particularly preferably
15 palladium acetate, palladium chloride or palladium trifluoroacetate, which is a low-cost palladium source. In the present invention, the structure of the above-mentioned metal compound is not particularly limited, and an active complex catalyst may be a monomer, a dimer
20 and/or a polymer.

Further, in the present invention, as the ligand for the liquid phase homogeneous complex catalyst, it is possible to use a phosphorus compound. For example, it is not particularly limited as long as it is a phosphorus
25 ligand such as a phosphine, a phosphite, a phosphonite, a phosphinite or a phosphoramidite. Such a ligand may be a monodentate or a bidentate. The ligand is preferably a

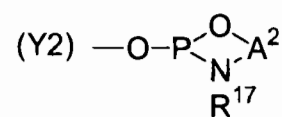
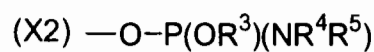
phosphorus compound having a P-O bond, and specifically, it is a phosphite or a phosphoramidite, particularly preferably a bidentate phosphite or a phosphoramidite. The reason is that in the isomerization reaction which goes through a π -allyl intermediate, a ligand having a low electron density accelerates the improvement of the reaction rate. Therefore, the phosphorus compound having a low electron density and a P-O bond, is preferred. Further, although one type of ligand is usually used, in the present invention, it is also possible to combine at least 2 types of phosphorus ligands. Moreover, as the case requires, it is possible to combine other ligands within a range where they do not deteriorate the effect of the present invention.

When the phosphorus compound having a P-O bond is used as a ligand in the present invention, the compounds represented by the following formulae (1) to (5) and formulae (6-1) to (6-7) may be mentioned. Further, in the present invention, although one type of ligand is usually used, it is also possible to combine at least 2 types of phosphorus ligands. Moreover, as the case requires, it is possible to combine other ligands within a range where they do not deteriorate the effect of the present invention.

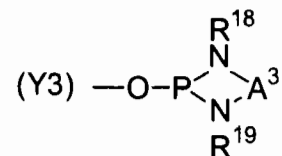
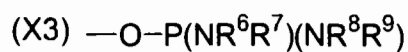
(1) RX



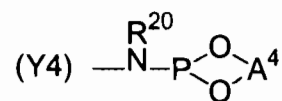
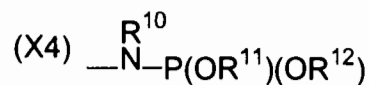
(2) R'Y



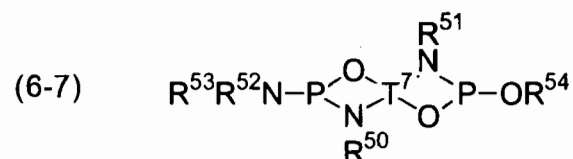
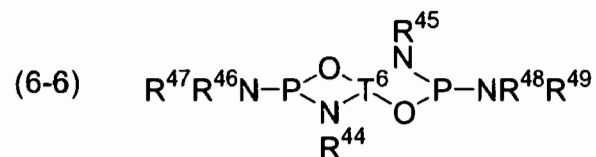
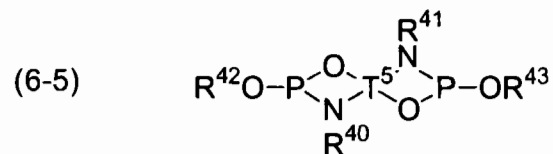
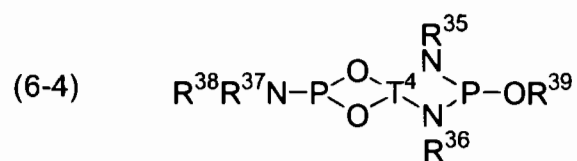
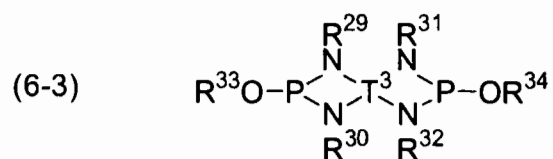
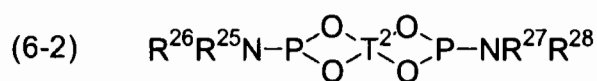
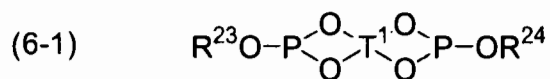
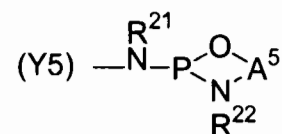
(3) X'—A—X''



(4) X'''—A'—Y'



(5) Y''—A''—Y'''



In the above formulae (1) to (5), X to X''' may be selected from (X1) to (X5), and Y to Y''' may optionally be selected from (Y1) to (Y5).

In the above (X1) to (X5), (Y1) to (Y5) and the
5 formulae (6-1) to (6-7), each of R, R' and R¹ to R⁵⁴ is independently an alkyl group, an alkoxy group, a cycloalkyl group, an aryloxy group, an alkylaryloxy group, an amino group or an aryl group, which may further contain a substituent group. When each of R, R' and R¹
10 to R⁵⁴ is an alkyl group or a substituent group having an alkyl structure (such as an alkyl group in an alkylaryloxy group), the number of carbon atoms in the alkyl group or the alkyl structure is usually from 1 to 20, preferably from 1 to 14. Specifically, a methyl
15 group, an ethyl group, a n-propyl group, an i-propyl group, a n-butyl group, an i-butyl group, a sec-butyl group, a t-butyl group, a pentyl group, a hexyl group, an octyl group or a decyl group. Further, the alkyl group or the alkyl structure may further contain a substituent
20 group. The substituent group may, for example, be a C₁₋₁₀ alkoxy group, a C₆₋₁₀ aryl group, an amino group, a cyano group, a C₂₋₁₀ ester group, a hydroxyl group or a halogen atom.

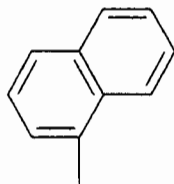
Further, when each of R, R' and R¹ to R⁵⁴ is an aryl
25 group or a substituent group having an aryl structure, the number of carbon atoms in the aryl group or the aryl structure is usually from 6 to 20, preferably from 6 to

14. The aryl group or the aryl structure may further contain a substituent group. The substituent group may, for example, be a hydrogen atom, a C₁₋₂₀ alkyl group, a C₁₋₁₀ alkoxy group, a C₃₋₂₀ cycloalkyl group, a C₆₋₂₀ aryl group, a C₆₋₂₀ aryloxy group, a C₆₋₂₀ alkylaryl group, a C₆₋₂₀ alkylaryloxy group, a C₆₋₂₀ arylalkyl group, a C₆₋₂₀ arylalkoxyl group, a cyano group, an ester group, a hydroxy group or a halogen atom.

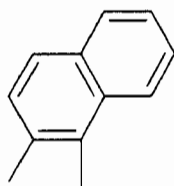
When each of R, R' and R¹ to R⁵⁴ is aryl group, specific examples may be a phenyl group, a 2-methylphenyl group, a 3-methylphenyl group, a 4-methylphenyl group, a 2,3-dimethylphenyl group, a 2,4-dimethylphenyl group, a 2,5-dimethylphenyl group, a 2,6-dimethylphenyl group, a 2-ethylphenyl group, a 2-isopropylphenyl group, a 2-
 15 butylphenyl group, a 2,4-di-t-butylphenyl group, a 2-chlorophenyl group, a 3-chlorophenyl group, a 4-chlorophenyl group, a 2,3-dichlorophenyl group, a 2,4-dichlorophenyl group, a 2,5-dichlorophenyl group, a 3,4-dichlorophenyl group, a 3,5-dichlorophenyl group, a 4-
 20 trifluoromethylphenyl group, a 2-methoxyphenyl group, a 3-methoxyphenyl group, a 4-methoxyphenyl group, a 3,5-dimethoxyphenyl group, a 4-cyanophenyl group, a 4-nitrophenyl group, a trifluoromethyl group, a pentafluoroethyl group, a pentafluorophenyl group, and
 25 the following groups (C-1) to (C-8).



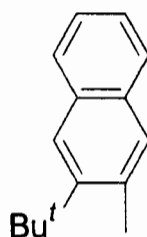
(C-1)



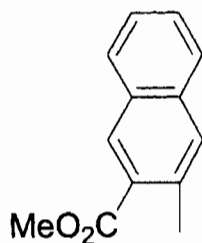
(C-2)



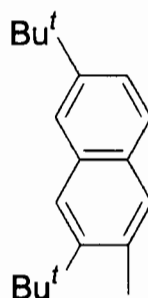
(C-3)



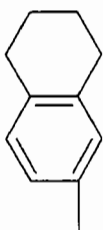
(C-4)



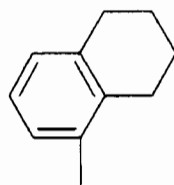
(C-5)



(C-6)



(C-7)



(C-8)

In the formulae (1) to (5) and (Y1) to (Y5), each of A to A" and A¹ to A⁵ is independently a C₁₋₂₀ alkylene group which may have a substituent group, a C₆₋₃₀ arylene group which may have a substituent group or a diarylene group of Ar¹-(Q¹)_n-Ar² which may have a divalent linking

group in the middle (wherein each of Ar^1 and Ar^2 is independently a C_{6-18} arylene group which may have a substituent group).

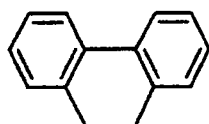
In the formulae (6-1) to (6-7), each of T^1 to T^7 is
 5 independently a carbon atom, an alkane tetrayl group, a benzene tetrayl group or a tetravalent group represented by $\text{T}^8-(\text{Q}^2)_n-\text{T}^9$ which may have a substituent. Each of T^8 and T^9 is independently a trivalent group selected from a C_{1-10} alkanetriyl group and a C_{6-15} benzenetriyl group,
 10 which may have a substituent group. Each of Q^1 and Q^2 is independently $-\text{CR}^{55}\text{R}^{56}-$, $-\text{O}-$, $-\text{S}-$ or $-\text{CO}-$, n is 0 or 1, and each of R^{55} and R^{56} is independently a hydrogen atom, a C_{1-10} alkyl group or a C_{6-20} aryl group, which may have a substituent group.

15 Further, when each of A to A'' and A^1 to A^5 is an alkylene group, the alkylene group may, for example, be a tetramethylethylene group or a dimethylpropylene group. Further, when each of A to A'' , and A^1 to A^5 is an alkylene group which may have a substituent group, the
 20 substituent group may, for example, be a C_{1-10} alkoxy group, a C_{6-20} aryl group, an amino group, a cyano group, an amide group or a trifluoromethyl group. Further, when each of A to A'' , and A^1 to A^5 is an arylene group which may have a substituent group, the arylene group may, for
 25 example, be a phenylene group or a naphthylene group. The substituent group may, for example, be a C_{1-10} alkoxy group, a C_{6-20} aryl group, an amino group, a cyano group,

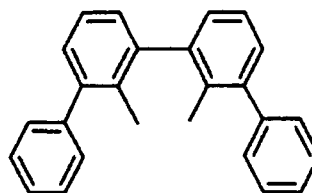
an amide group or a trifluoromethyl group.

Further, when each of A to A", and A¹ to A⁵ is a diarylene group of Ar¹-(Q¹)_n-Ar² which may have a divalent linking group in the middle, each of Ar¹ and Ar² is
 5 independently a C₆₋₁₈ arylene group which may have a substituent group, and the number of carbon atoms in the arylene group is from 6 to 24, further preferably from 6 to 16. Specific examples for the preferred substituent group may, for example, be a C₆₋₂₀ aryl group, an amino
 10 group, a cyano group, an amide group or a trifluoromethyl group.

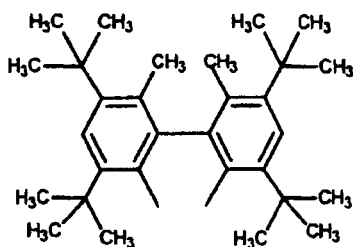
Further, specific examples for A to A" and A¹ to A⁵ may, for example, be -(CH₂)₂-, -(CH₂)₃-, -(CH₂)₄-,
 -(CH₂)₅-, -(CH₂)₆-, -CH(CH₃)-CH(CH₃)-, -CH(CH₃)CH₂CH(CH₃)-,
 15 -C(CH₃)₂-C(CH₃)₂-, -C(CH₃)₂-CH₂-C(CH₃)₂- and the following groups (A-1) to (A-48).



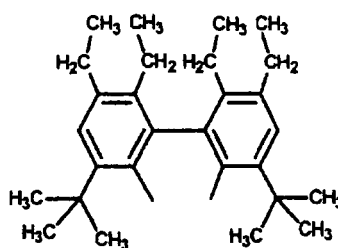
(A-1)



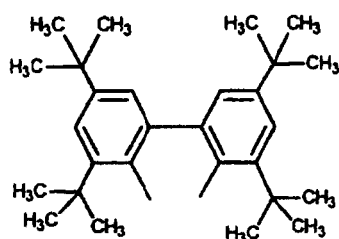
(A-2)



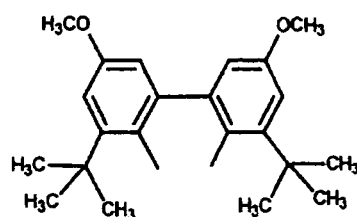
(A-3)



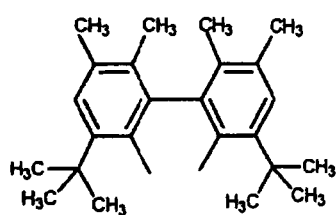
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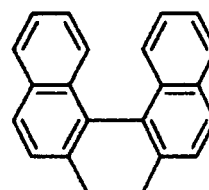
(A-5)



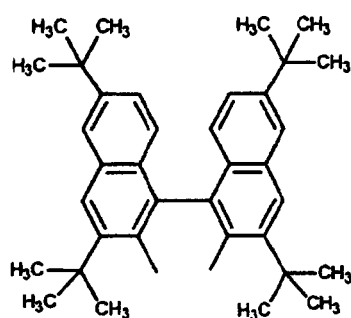
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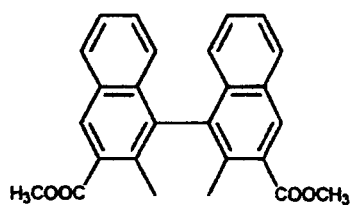
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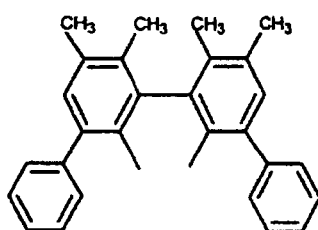
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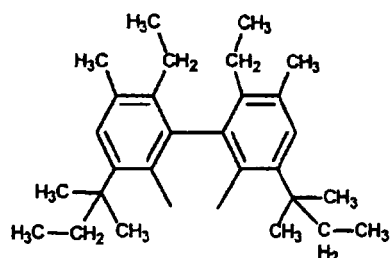
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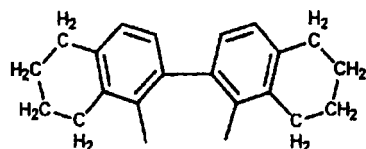
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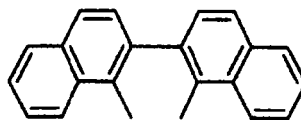
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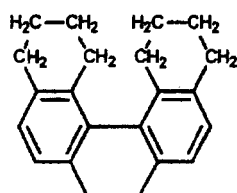
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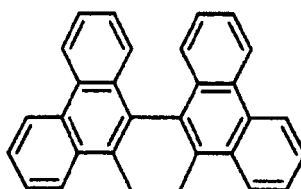
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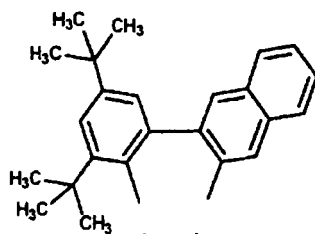
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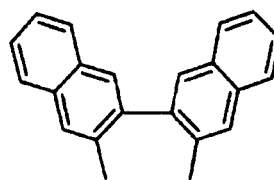
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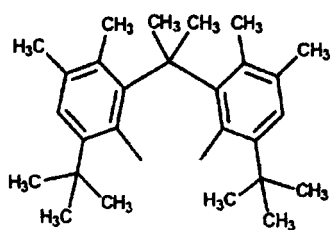
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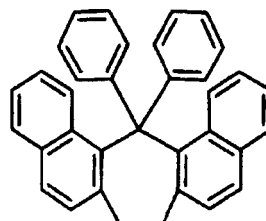
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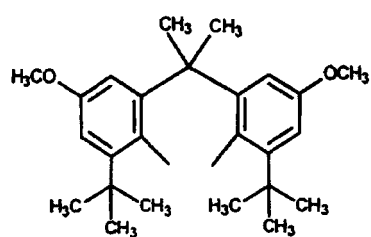
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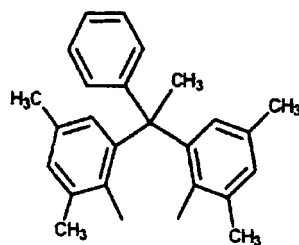
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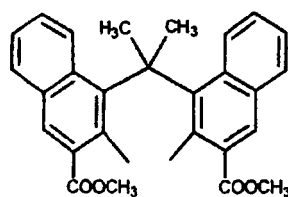
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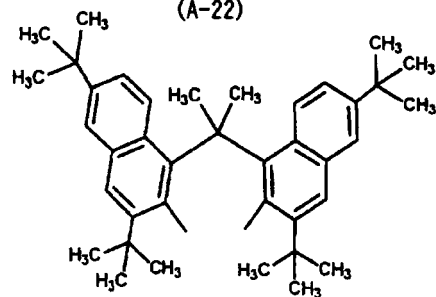
(A-21)



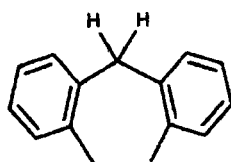
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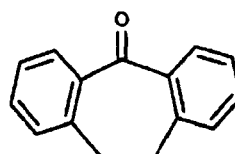
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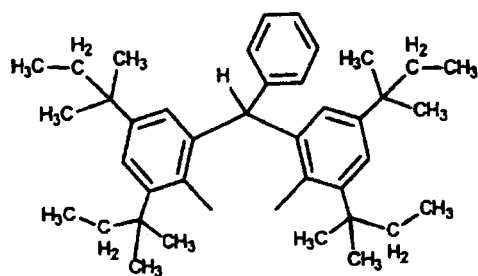
(A-24)



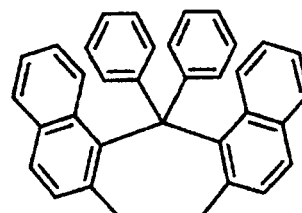
(A-25)



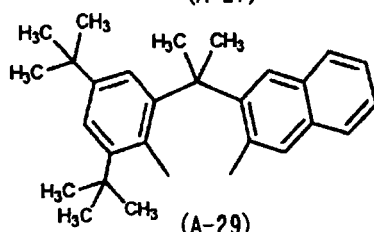
(A-26)



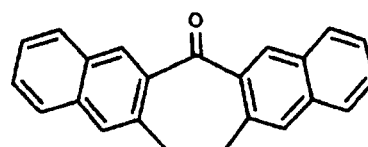
(A-27)



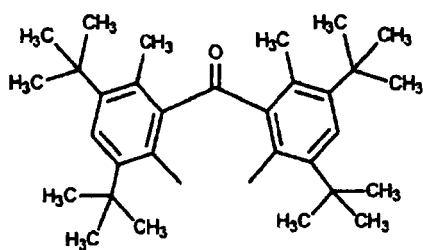
(A-28)



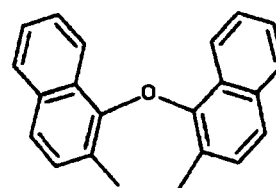
(A-29)



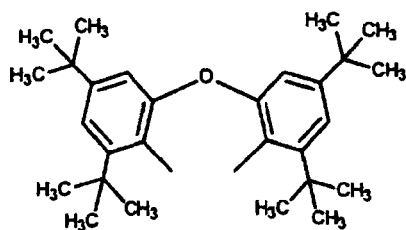
(A-30)



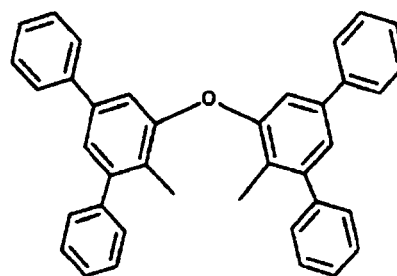
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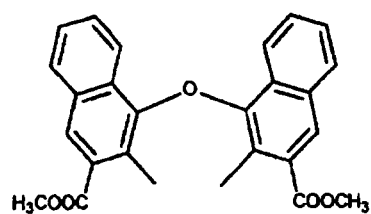
(A-32)



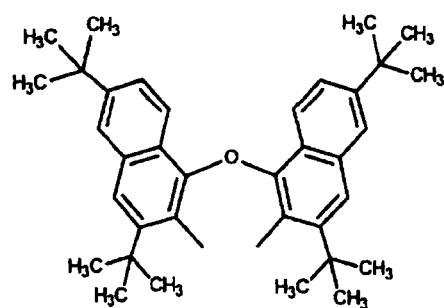
(A-33)



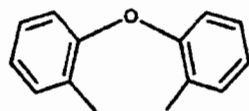
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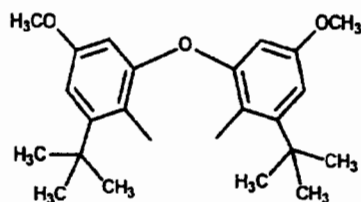
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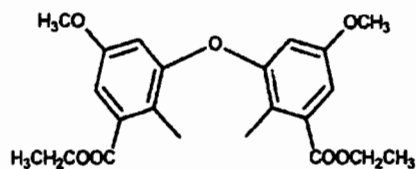
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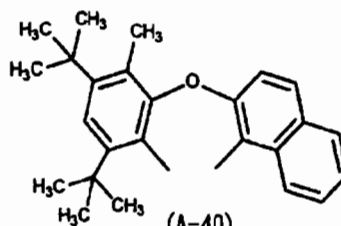
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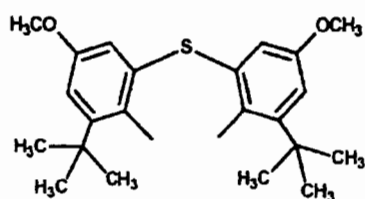
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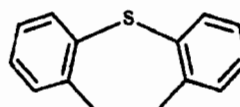
(A-39)



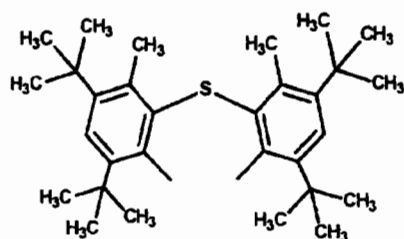
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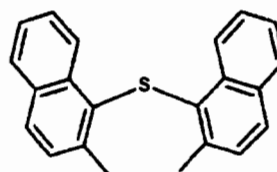
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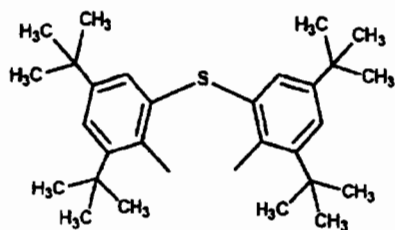
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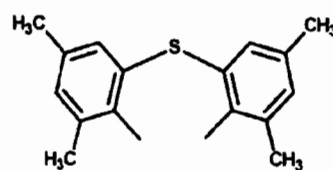
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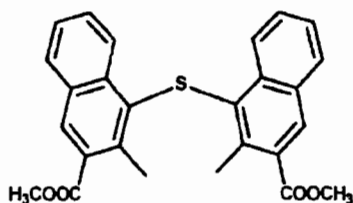
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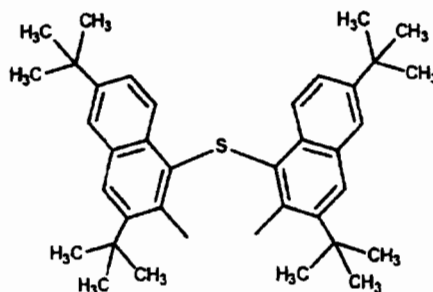
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(A-46)



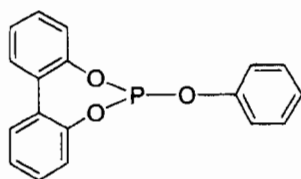
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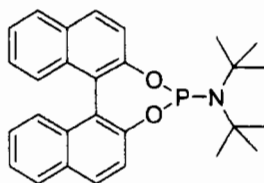
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Specific preferred examples for compounds of the

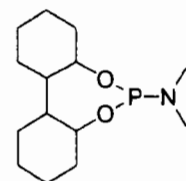
formulae (1) to (5) and the formulae (6-1) to (6-7), which represent the ligand of the present invention may, for example, be the following monodentate ligands (L-1) to (L-16) and multidentate ligands (L-17) to (L-44), and
5 the particularly preferred examples may, for example, be (L-17) to (L-36).



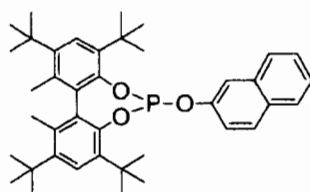
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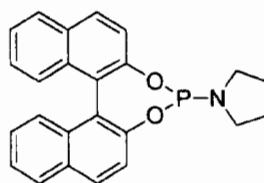
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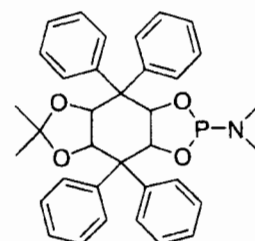
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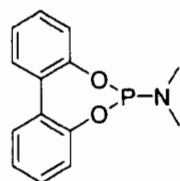
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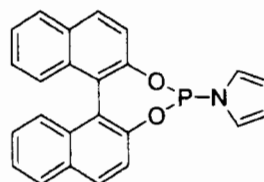
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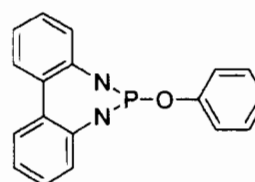
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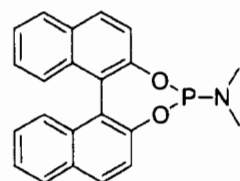
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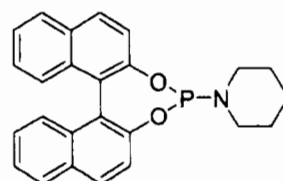
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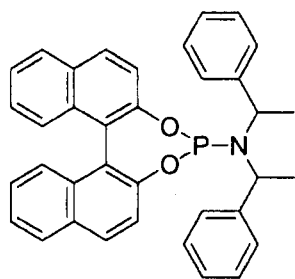
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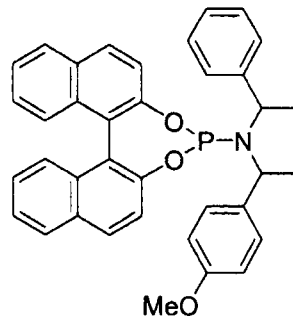
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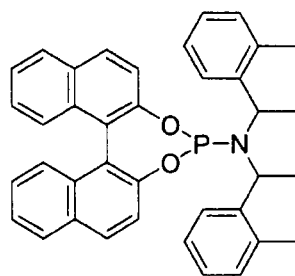
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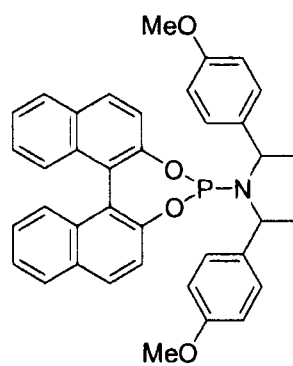
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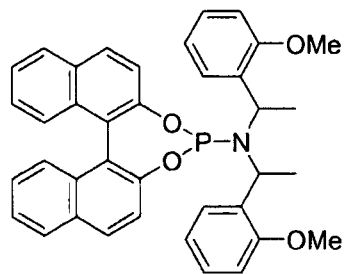
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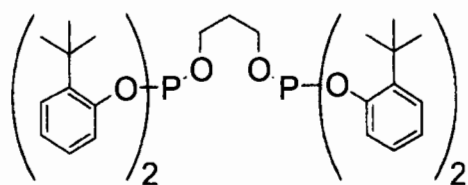
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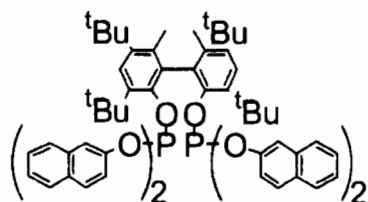
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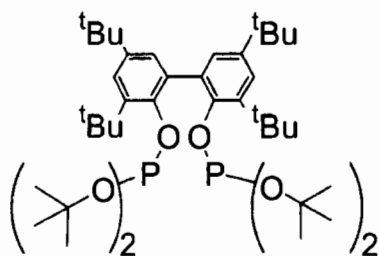
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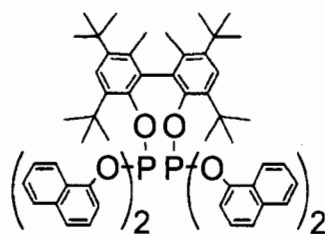
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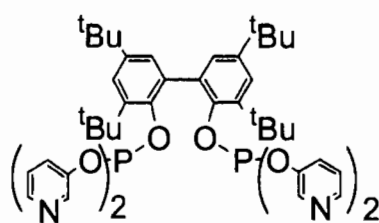
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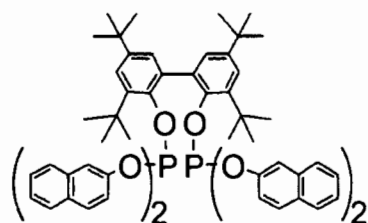
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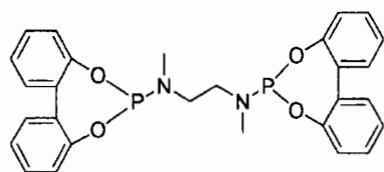
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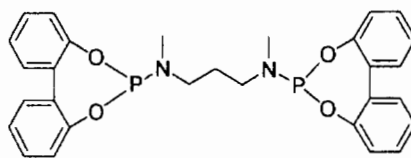
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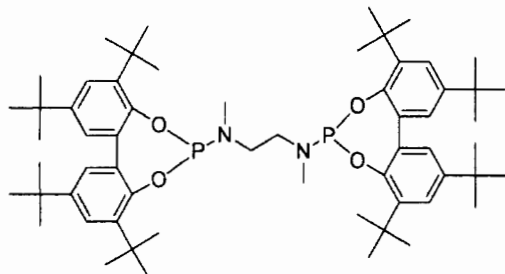
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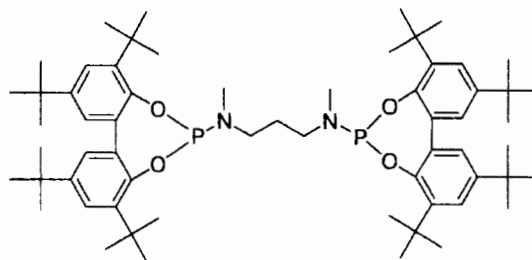
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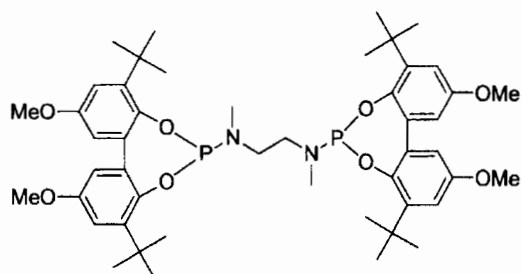
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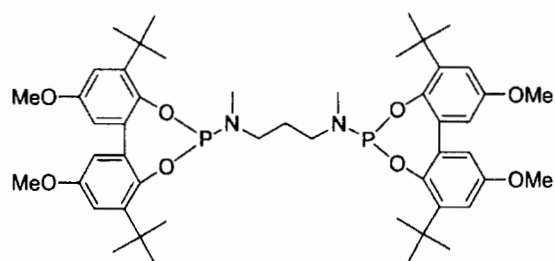
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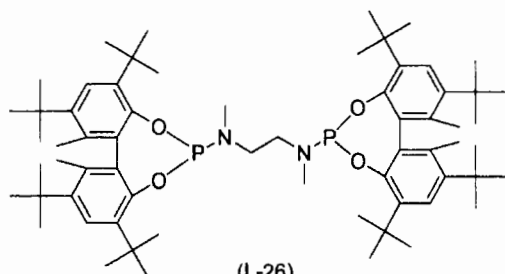
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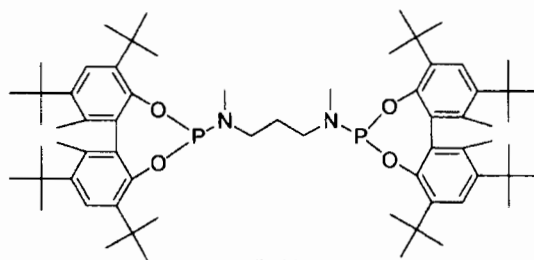
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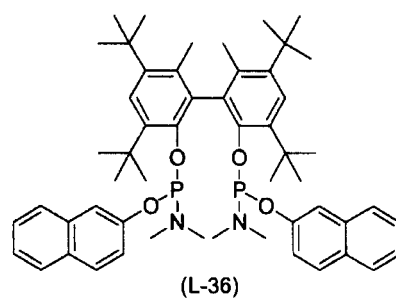
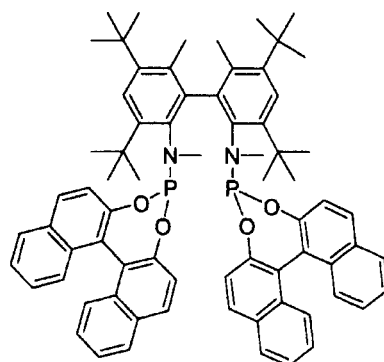
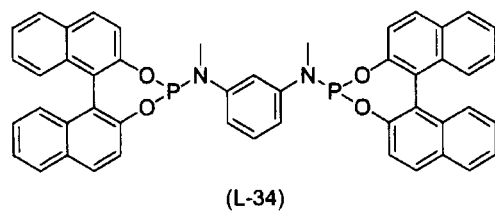
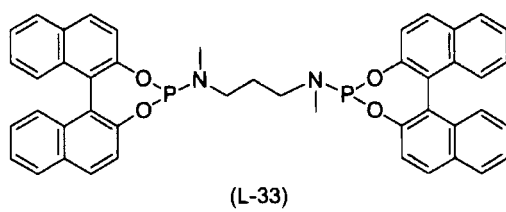
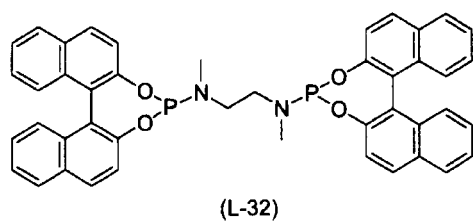
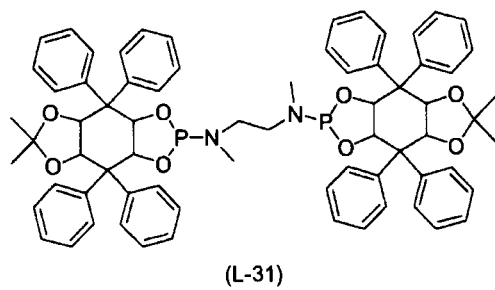
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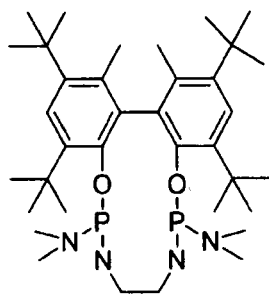


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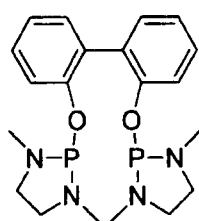


(L-30)

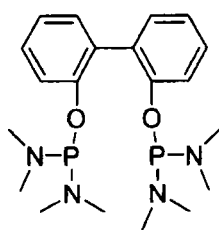




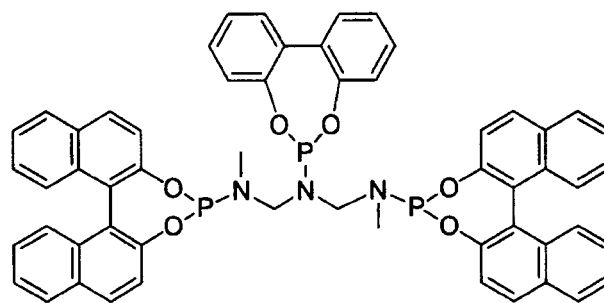
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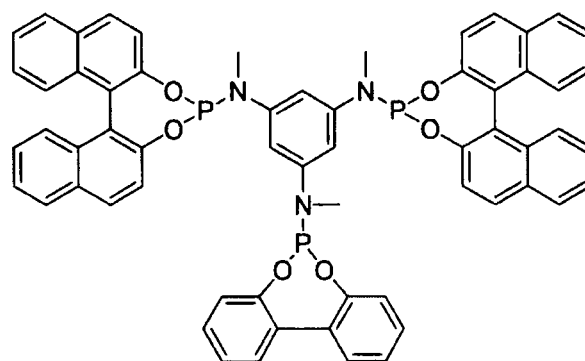
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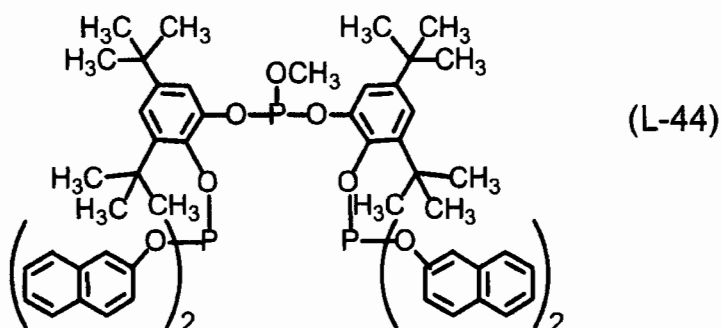
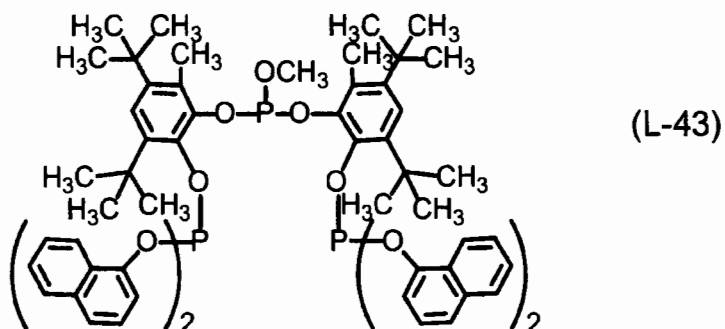
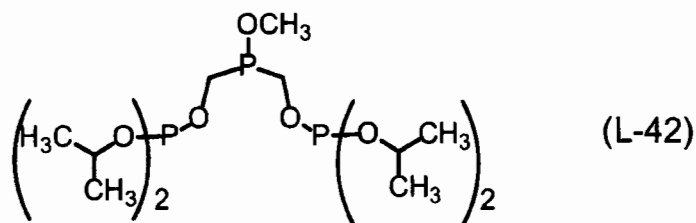
(L-39)



(L-40)



(L-41)



Among the specific examples for a phosphite and a phosphoramidite, preferred are L20 to L44, and particularly preferred are L21 to L30. The reason why
 5 they are preferred is that the heat stability of the ligand is relatively high and disappearance of the ligand by deactivation of a catalyst active species is relatively low.

In the present invention, the amount of the
 10 homogeneous complex catalyst to be used for isomerization of the diacetoxyallyl compound is, as converted into the metal amount in the 3,4-diacetoxyallyl compound-

containing liquid, preferably from 0.001 to 1,000 wtppm, more preferably from 0.01 to 100 wtppm, particularly preferably from 0.1 to 10 wtppm, based on the 3,4-diacetoxyallyl compound-containing liquid. As the amount
5 of the catalyst becomes large, the reaction rate becomes high, whereby it is possible to reduce the size of the reactor, and it is possible to reduce the equipment cost. Further, as the amount of the catalyst becomes small, it is possible to reduce the ligand cost.

10 Further, with respect to the amount of the ligand, the molar ratio of the phosphorus atom in the ligand is preferably from 0.1 to 1,000, more preferably from 1 to 100, particularly preferably from 1 to 10, to the transition metal in the complex catalyst. As the amount
15 of the ligand becomes large, the reaction rate increases. On the other hand, as the amount of the ligand becomes small, it is possible to reduce the catalyst cost.

The reaction temperature during the isomerization reaction, is preferably from 40 to 200°C, more preferably
20 from 80 to 180°C, particularly preferably from 100 to 160°C. The higher the reaction temperature, the higher the reaction rate, and a small reactor will be sufficient, whereby it is possible to reduce the equipment cost. On the other hand, the lower the
25 reaction temperature, the slower the catalyst deterioration, whereby it is possible to reduce the catalyst cost.

Further, it is possible to improve the stability of the catalyst or the reaction rate by combining another phosphorus compound as a promoter in addition to the above catalyst ligand, in the reactor. The phosphorus compound to be used here is not particularly limited as long as it is one wherein 3 substituent groups are bonded to the phosphorus atom. For example, it is preferably a triaryl phosphine such as triphenyl phosphine, tri(2-methylphenyl)phosphine, tri(4-methylphenyl)phosphine, tri(2-methoxyphenyl)phosphine or tri(4-methoxyphenyl)phosphine; a diarylalkyl phosphine such as diphenylmethyl phosphine, diphenylethyl phosphine or diphenylpropyl phosphine; a dialkylaryl phosphine such as dimethylphenyl phosphine or diethylphenyl phosphine; or a trialkylphosphine such as trioctyl phosphine or tributyl phosphine, more preferably a triaryl phosphine such as triphenyl phosphine, tri(2-methylphenyl)phosphine, tri(4-methylphenyl)phosphine, tri(2-methoxyphenyl)phosphine or tri(4-methoxyphenyl)phosphine, particularly preferably triphenyl phosphine.

With respect to the amount of another phosphorus compound as a promoter other than such ligands, the molar ratio of the phosphorus atom in the phosphorus compound is preferably from 1 to 10,000, more preferably from 10 to 2,000, particularly preferably from 50 to 500, to the amount of the transition metal in the complex catalyst. If the amount of the phosphorus compound is too small,

the reaction rate will decrease, and if it is too large, the cost will increase. Within such a range, it is acceptable to use another phosphorus compound alone or to use several phosphorus compounds as a mixture.

5 With respect to the reactor to be used for the isomerization reaction in the present invention, it is allowed to use one in a form which is used for a common liquid-phase reaction. Preferred is a tube reactor or a tank reactor, and such a reactor may be used alone or in
10 a multistage. Particularly preferred is a tank reactor or a multistage tank reactor, and a multistage reactor having a perforated tray is further preferred.

 In the present invention, before isomerizing the 3,4-diacetoxyallyl compound to the 1,4-diacetoxyallyl
15 compound by the catalyst, it is required to contact the 3,4-diacetoxyallyl compound-containing liquid with the phosphorus compound, as mentioned above. Among phosphorus compounds, preferred are the organic phosphorus compounds, and among the organic phosphorus
20 compounds, further preferred are an organic phosphite, an organic phosphoramidite and an organic phosphine, particularly preferred is an organic phosphine. As the organic phosphine, it is possible to use at least a monodentate, a bidentate or a tridentate organic
25 phosphine, and preferred is a monodentate organic phosphine having at least two aryl groups. Such a phosphine is not particularly limited, and it is possible

to use a marketed product. Specifically, preferred is an alkyl phosphine such as trimethyl phosphine, triethyl phosphine, tripropyl phosphine, tributyl phosphine, tripentyl phosphine, trihexyl phosphine, triheptyl phosphine, trioctyl phosphine, tricyclopentyl phosphine, tricyclohexyl phosphine or tricycloheptyl phosphine; or a phenyl phosphine such as triphenyl phosphine, diphenylmethyl phosphine, diphenylethyl phosphine, diphenylbutyl phosphine, dimethylphenyl phosphine, diethylphenyl phosphine, dibutylphenyl phosphine, tris(tolyl)phosphine or 1,2-bis(diphenylphosphino)ethane, and further preferred is a phenyl phosphine. Among the phenyl phosphines, particularly preferred is triphenyl phosphine, diphenylmethyl phosphine, diphenylethyl phosphine, diphenylbutyl phosphine or tris(tolyl) phosphine, and the most preferred is triphenyl phosphine. Further, although one type of the phosphorus compound is usually used, in the present invention, it is possible to combine at least two types of the phosphorus compounds. Moreover, as the case requires, it is possible to use such a phosphorus compound in combination with other compounds as long as such combination does not deteriorate the effect of the present invention.

The temperature during the contact of the 3,4 diacetoxiallyl compound with the above phosphorus compound before isomerizing it to the 1,4-diacetoxiallyl compound by the catalyst, is usually at least 60°C,

preferably at least 80°C, particularly preferably at least 100°C. On the other hand, the temperature during the contact with the phosphorus compound is usually at most 200°C, preferably at most 180°C, particularly
5 preferably at most 160°C. The higher the temperature, the higher the effect for reducing the catalyst deterioration component by the phosphorus compound. Further, the lower the temperature, the lower the energy cost for heating the phosphorus compound.

10 Further, the contacting time is preferably from 1 minute to 100 hours, more preferably from 10 minutes to 10 hours, particularly preferably from 30 minutes to 5 hours. As the contacting time becomes long, it is possible to sufficiently remove the catalyst
15 deterioration component. Further, as the contacting time becomes short, the operation efficiency of the process becomes high.

Further, it is possible to use the phosphorus compound, by wt%, in a range of from 0.00001 to 10 wt%,
20 more preferably from 0.0001 to 1 wt%, particularly preferably from 0.001 to 0.1 wt%, based on the 3,4-diacetoxyallyl compound-containing liquid. As the amount of the phosphorus compound to be used is large, it is possible to obtain the sufficient removal effect of the
25 catalyst deterioration component. On the other hand, if the amount of the phosphorus compound to be used is small, it is possible to reduce the cost of the

phosphorus compound.

In the present invention, the method for contacting the 3,4-diacetoxyallyl compound with the phosphorus compound before isomerizing the 3,4-diacetoxyallyl compound to the 1,4-diacetoxyallyl compound by the catalyst is not particularly limited. However, usually, it may, for example, be (1) a method wherein the 3,4-diacetoxyallyl compound and the phosphorus compound are put into a container, followed by stirring and mixing, (2) a method wherein a 3,4-diacetoxyallyl compound solution containing the phosphorus compound is separately prepared, and the 3,4-diacetoxyallyl compound and the 3,4-diacetoxyallyl compound solution containing the phosphorus compound are put into a container, followed by stirring and mixing, or (3) a method wherein the 3,4-diacetoxyallyl compound and the 3,4-diacetoxyallyl compound solution containing the phosphorus compound are merged from the respective pipes into one pipe as a stream to contact them to each other, and mixed. Further, it is also possible to mix them at the desired temperature for the desired period of time after they are contacted to each other. From the viewpoint of productivity, a continuous process is preferred. Therefore, the method for contacting is preferably the above (3) wherein the 3,4-diacetoxyallyl compound and the 3,4-diacetoxyallyl compound solution containing the phosphorus compound are merged from the respective lines

(pipes) into one line (pipe) as a stream to contact them to each other and mixed.

The contacting method for the phosphorus compound with the 3,4-diacetoxyallyl compound may be either batch or continuous, but from the viewpoint of the operation efficiency, a continuous circulation system is particularly preferred. The phosphorus compound can be separated by distillation before the isomerization reaction and can be recycled, but from the viewpoint of energy efficiency, it is desired to be separated after the isomerization reaction by e.g. distillation from the 1,4-diacetoxyallyl compound formed in the same manner as for the catalyst component. The phosphorus compound separated here, may be recycled, but usually, it is discharged as a waste liquid out of the process system.

In the present invention, in the reaction liquid obtained from the isomerization reaction, the unreacted 3,4-diacetoxyallyl compound is present in addition to the 1,4-diacetoxyallyl compound as the reaction product, and it is possible to separate the 3,4-diacetoxyallyl compound-containing liquid from the reaction liquid by e.g. distillation. The pressure of the distillation column at that time may optionally be set, but to lower the temperature at the bottom of the column, the pressure at the top of the column is preferably from 1 to 760 mmHg. Further, the pressure at the top of the column is more preferably from 5 to 200 mmHg, particularly

preferably from 10 to 100 mmHg. If the pressure at the top of the column is too low, in order to maintain the pressure, a high cost will be needed, and the distillation column itself will have to be large, whereby an installation cost for the process will increase. Further, if the pressure at the top of the column is too high, the temperature at the bottom of the column will also be high, whereby a steam cost will increase. The temperature at the top of the column is usually from 0 to 200°C, preferably from 20 to 160°C, more preferably from 40 to 140°C. If the temperature at the top of the column is too low, a specific device such as a cooler will be needed, which adds to the cost. Further, if the temperature is too high, the temperature at the bottom of the column will also be high, whereby the steam cost will increase. A reflux ratio may be from 1 to 100, preferably from 1 to 10. If the reflux ratio is too small, separation ability tends to be deteriorated, and if the reflux ratio is too large, the amount of heat needed tends to increase thus leading to an increase of the cost. With respect to the amount of the distillation from the top of the column, it is desired to distill the total amount of the 3,4-diacetoxyallyl compound and the low boiling point compounds from the liquid introduced into the distillation column, which contains the 3,4-diacetoxyallyl compound, and the 1,4-diacetoxyallyl compound, the low boiling point compounds and the high

boiling point compounds. Further, when the 3,4-diacetoxyallyl compound-containing liquid is to be withdrawn from the side-portion, and the low boiling point compounds are to be distilled from the top of the column, it is preferred to withdraw the content of the 3,4-diacetoxyallyl compound in the feed liquid from the side-portion, and distill the low boiling point compounds in the feed liquid from the top of the column.

By introducing the 3,4-diacetoxyallyl compound-containing liquid obtained by distillation separation into an isomerization reactor, it is possible to isomerize the unreacted 3,4-diacetoxyallyl compound to the 1,4-diacetoxyallyl compound. The 3,4-diacetoxyallyl compound-containing liquid which is recirculated to the reactor, is preferably kept at the temperature at the time when it was obtained by the distillation separation or the temperature inside the isomerization reactor. However, irrespective of the temperature, pressure, etc. of recirculation, it is possible to carry out the isomerization for the 1,4-diacetoxyallyl compound under the isomerization reaction conditions. Further, such isomerization reaction conditions may be the same conditions as mentioned above.

The 1,4-diacetoxyallyl compound obtained by the isomerization reaction will be left as it is, or after further purification by e.g. distillation, it will be hydrogenated and transformed into a 1,4-diacetoxybutane

compound which may have a substituent group, in the presence of a transition metal catalyst. The transition metal catalyst to be used here may be a hydrogenating catalyst as a commonly marketed product, but it is preferably a nickel catalyst or a catalyst containing a noble metal such as palladium or ruthenium. In the presence of such a hydrogenating catalyst, and at the temperature in a range of from 40 to 180°C, it is possible to carry out the hydrogenation in such a manner that hydrogen and the 1,4-diacetoxyallyl compound-containing liquid are contacted to each other, under a pressure condition in a range of from atmospheric pressure to 15 MPa. If the reaction temperature is too high, the catalyst deterioration will proceed quickly, and if the reaction temperature is too low, the reaction rate will decrease. If the pressure is too low, the reaction rate will decrease, and if the pressure is too high, an expensive reactor will be required.

The 1,4-diacetoxybutane compound obtained by the hydrogenation reaction will be hydrolyzed by an acid catalyst or a basic material in the presence of water, and it will be transformed into a diol such as a 1,4-butanediol. As the catalyst, a solid acid catalyst is preferred, and it is particularly preferred to use a cation-exchange resin, since the hydrolysis proceeds quickly, and there will be less production of a by-product such as tetrahydrofuran. Specifically, such a

resin may be a sulfonic acid type strong acidic cation-exchange resin having a copolymer of styrene and divinyl benzene, as a parent body. It may be a gel type or a porous type. The reaction is usually carried out under a temperature condition of from 30 to 110°C, preferably from 40 to 90°C. If the temperature is too low, the hydrolysis rate will decrease, whereby an expensive large reactor will be required. If the temperature is too high, a by-product such as tetrahydrofuran will increase, whereby the yield of the 1,4-butanediol will decrease. The amount of water to be used is usually in a range of from 2 to 100 mol, preferably from 4 to 50 mol, per one mol of the 1,4-diacetoxybutane. If the amount of water is too small, the reaction rate will decrease, whereby an expensive large reactor will be required. Further, if the amount of water is too large, the large amount of energy will be needed when removing water from the 1,4-butanediol after the hydrolysis, whereby the energy cost will increase.

20

EXAMPLES

Now, the present invention will be described in further detail with reference to Examples, but the present invention is by no means restricted by the following Examples.

25

Further, in the following Examples, analyses of 3,4-diacetoxy-1-butene and 1,4-diacetoxy-2-butene were

carried out by gas chromatography in accordance with an internal standard method. Dodecane was used as the internal standard material.

REFERENCE EXAMPLE 1: Step of Acetoxylation Reaction of
5 Butadiene

In the presence of 1 kg of a Pd-Te catalyst, 0.21 kg/hr of butadiene, 2.94 kg/hr of acetic acid and 0.34 kg/hr of a gas mixture of 6 vol% oxygen/94 vol% nitrogen were introduced into a reactor and subjected to an
10 acetoxylation reaction under conditions of 80°C and 6 MPa, to obtain a liquid mixture comprising 81 wt% of 1,4-diacetoxy-2-butene, 9 wt% of 3,4-diacetoxy-1-butene, 2 wt% of 3-hydroxy-4-acetoxy-1-butene and 3 wt% of acetic acid, and additionally, 3 wt% of low boiling point
15 compounds and 2 wt% of high boiling point compounds.

REFERENCE EXAMPLE 2: Separation of 3,4-Diacetoxy-1-Butene-Containing Liquid

From 11 L of the liquid mixture obtained in the Reference Example 1, the 3,4-diacetoxy-1-butene-
20 containing liquid was separated by continuous distillation. Here, for the distillation, an Oldershaw distillation column having 20 plates was used. While maintaining the pressure at the top of the column to be 20 mmHg, the reflux ratio to be 3, the temperature at the
25 top of the column to be 95°C and the temperature at the bottom of the column to be 151°C, the liquid was continuously introduced with a flow rate of 150 cc/hr at

the position of 10 plates from the bottom of the column, whereby from the top of the column, 27 cc/hr was continuously distilled, and from the bottom of the column, 123 cc/hr was continuously withdrawn. By such
5 continuous distillation, a liquid containing 1,4-diacetoxy-2-butene was obtained as the bottoms from the bottom of the column, and a 3,4-diacetoxy-1-butene-containing liquid was obtained as distillate from the top of the column. The obtained 3,4-diacetoxy-1-butene-
10 containing liquid was a liquid mixture comprising 45 wt% of 3,4-diacetoxy-1-butene, 11 wt% of 3-hydroxy-4-acetoxy-1-butene and 22 wt% of acetic acid, and additionally, 20 wt% of components having lower boiling points than the 3,4-diacetoxy-1-butene and 2 wt% of components having
15 higher boiling points than the 3,4-diacetoxy-1-butene. Further, the content of the 1,4-diacetoxy-2-butene in the 3,4-diacetoxy-1-butene-containing liquid was at most 1 wt%.

REFERENCE EXAMPLE 3: Purification and Distillation of
20 3,4-Diacetoxy-1-Butene-Containing Liquid

From 1 L of the 3,4-diacetoxy-1-butene-containing liquid obtained in Reference Example 2, most of the low boiling point compounds were separated by continuous distillation. Here, for the distillation, an Oldershaw
25 distillation column having 40 plates was used. While maintaining the pressure at the top of the column to be 100 mmHg, the reflux ratio to be 1, the temperature at

the top of the column to be 95°C and the temperature at the bottom of the column to be 148°C, the liquid was continuously introduced with a flow rate of 100 cc/hr at the position of 20 plates from the bottom of the column, whereby from the top of the column, 41 cc/hr was continuously distilled, and from the bottom of the column, 59 cc/hr was continuously withdrawn. By such continuous distillation, low boiling point compounds were obtained as distillate from the top of the column. The distillate comprises 59 wt% of acetic acid, 1.6 wt% of 3,4-diacetoxy-1-butene (which corresponds to 1.5 wt% of the amount of the 3,4-diacetoxyallyl compound to be introduced into a distillation column), and additionally, 39.4 wt% of components having lower boiling points than the 3,4-diacetoxy-1-butene. Further, from the liquid withdrawn from the bottom of the column, a 3,4-diacetoxy-1-butene-containing liquid comprising 72 wt% of the 3,4-diacetoxy-1-butene and 18 wt% of 3-hydroxy-4-acetoxy-1-butene, and additionally, 6 wt% of low boiling point compounds and 4 wt% of high boiling point compounds, was obtained.

REFERENCE EXAMPLE 4: Preparation of Catalyst

Under the nitrogen gas atmosphere, in a glass Schlenk flask, 10.5 mg of palladium acetate, 96.3 mg of a phosphite ligand represented by the above L21 and 49.8 mg of triphenyl phosphine were added to 41.3 g of the 3,4-diacetoxy-1-butene-containing liquid obtained in

Reference Example 3. Such a liquid mixture was heated at 80°C for 1 hour and dissolved completely to obtain a catalyst solution.

REFERENCE EXAMPLE 5: Preparation of Catalyst

5 Under the nitrogen gas atmosphere, in a glass Schlenk flask, 5.9 mg of palladium acetate, 56.9 mg of a ligand represented by the above L29 and 30.3 mg of triphenyl phosphine were added to 13.99 g of toluene. Such a mixture was heated at 120°C for 20 minutes and dissolved
10 completely to obtain a catalyst solution.

REFERENCE EXAMPLE 6: Preparation of Catalyst

Under the nitrogen gas atmosphere, in a glass Schlenk flask, 5.5 mg of palladium acetate, 43.0 mg of a ligand represented by the above L30 and 25.8 mg of triphenyl
15 phosphine were added to 12.19 of toluene. Such a mixture was heated at 120°C for 20 minutes and dissolved completely to obtain a catalyst solution.

EXAMPLE 1

Into 1.5 cc of the 3,4-diacetoxy-1-butene-containing
20 liquid obtained in the above Reference Example 3 "Purification and Distillation of 3,4-Diacetoxy-1-Butene-Containing Liquid" (the purified 3,4-diacetoxy-1-butene comprising 72 wt% of the 3,4-diacetoxy-1-butene and 18 wt% of 3-hydroxy-4-acetoxy-1-butene, and additionally, 6
25 wt% of low boiling point compounds and 4 wt% of high boiling point compounds), 0.166 mg of triphenyl phosphine (0.0073 wt% based on the 3,4-diacetoxy-1-butene) was

added as 18 μ L of an acetic acid solution having a triphenyl phosphine concentration of 0.86%, followed by stirring at a temperature of 150°C for 3 hours.

Then, 1.5 cc of acetic acid was added to the Schlenk flask and mixed, and the mixture was heated at 130°C in an oil bath. 26 μ L of the catalyst solution prepared in Reference Example 4 was added thereto, in the nitrogen atmosphere, followed by heating and stirring at 130°C for 3 hours (the concentration of palladium in the reaction liquid was 1.0 wtppm). As a result of the analysis of the liquid after the isomerization reaction, by gas chromatography, the weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 45:55. Further, dodecane was used as the internal standard material. The results are shown in Table 1.

EXAMPLE 2

The operation was carried out in the same manner as in Example 1, except that the amount of triphenyl phosphine to be added was changed to 0.332 mg (0.0147 wt% based on the 3,4-diacetoxy-1-butene). As a result of the analysis of the liquid after the isomerization reaction, by gas chromatography, the weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 44:56. Further, dodecane was used as the internal standard material. The results are shown in Table 1.

EXAMPLE 3

The operation was carried out in the same manner as in Example 1, except that the stirring after the addition of triphenyl phosphine was carried out at a temperature of 150°C for 1 hour. As a result of the analysis of the liquid after the isomerization reaction, by gas chromatography, the weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 44:56. Further, dodecane was used as the internal standard material. The results are shown in Table 1.

EXAMPLE 4

The operation was carried out in the same manner as in Example 1, except that after the addition of 0.166 mg of triphenyl phosphine (0.0073 wt% based on the 3,4-diacetoxy-1-butene), stirring was carried out at a temperature of 30°C for 5 minutes. As a result of the analysis of the liquid after the isomerization reaction, by gas chromatography, the weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 40:60. Further, dodecane was used as the internal standard material. The results are shown in Table 1.

EXAMPLE 5

The operation was carried out in the same manner as in Example 1, except that triphenyl phosphine was changed to triphenyl phosphite, and the amount of the triphenyl

phosphite was 0.166 mg (0.0073 wt% based on the 3,4-diacetoxy-1-butene). As a result of the analysis of the liquid after the isomerization reaction, by gas chromatography, the weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 36:64. Further, dodecane was used as the internal standard material. The results are shown in Table 1.

EXAMPLE 6

10 Into 2.94 cc of the 3,4-diacetoxy-1-butene-containing liquid obtained in the above Reference Example 3 "Purification and Distillation of 3,4-Diacetoxy-1-Butene-Containing Liquid" (the purified 3,4-diacetoxy-1-butene comprising 72 wt% of the 3,4-diacetoxy-1-butene and 18
15 wt% of 3-hydroxy-4-acetoxy-1-butene, and additionally, 6 wt% of components having lower boiling points than the 3,4-diacetoxy-1-butene and 4 wt% of components having higher boiling points than the 3,4-diacetoxy-1-butene), 0.15 mg of triphenyl phosphine (0.0050 wt% based on the
20 3,4-diacetoxy-1-butene) was added as 8 μ L of an acetic acid solution having a triphenyl phosphine concentration of 0.86%, followed by stirring at a temperature of 150°C for 3 hours.

 Then, 0.06 cc of acetic acid was added to the Schlenk
25 flask and mixed, and the mixture was heated at 130°C in an oil bath. 18 μ L of the catalyst solution prepared in Reference Example 5 was added thereto, in the nitrogen

atmosphere, followed by heating and stirring at 130°C for 3 hours (the concentration of palladium in the reaction liquid was 1.0 wtppm). As a result of the analysis of the liquid after the isomerization reaction, by gas chromatography, the weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 49:53. Further, dodecane was used as the internal standard material. The results are shown in Table 2.

10 EXAMPLE 7

Into 2.94 cc of the 3,4-diacetoxy-1-butene-containing liquid obtained in the above Reference Example 3 "Purification and Distillation of 3,4-Diacetoxy-1-Butene-Containing Liquid" (the purified 3,4-diacetoxy-1-butene comprising 72 wt% of the 3,4-diacetoxy-1-butene and 18 wt% of 3-hydroxy-4-acetoxy-1-butene, and additionally, 6 wt% of components having lower boiling points than the 3,4-diacetoxy-1-butene and 4 wt% of components having higher boiling points than the 3,4-diacetoxy-1-butene), 0.15 mg of triphenyl phosphine (0.0050 wt% based on the 3,4-diacetoxy-1-butene) was added as 8 μ L of an acetic acid solution having a triphenyl phosphine concentration of 0.86%, followed by stirring at a temperature of 150°C for 3 hours.

25 Then, 0.06 cc of acetic acid was added to the Schlenk flask and mixed, and the mixture was heated at 130°C in an oil bath. 18 μ L of the catalyst solution prepared in

Reference Example 6 was added thereto, in the nitrogen atmosphere, followed by heating and stirring at 130°C for 4 hours (the concentration of palladium in the reaction liquid was 1.0 wtppm). As a result of the analysis of the liquid after the isomerization reaction, by gas chromatography, the weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 52:48. Further, dodecane was used as the internal standard material. The results are shown in Table 2.

COMPARATIVE EXAMPLE 1

The operation was carried out in the same manner as in Example 1, except that 7.8 mg of an anion-exchange resin (Diaion, WA20) was added instead of triphenyl phosphine (0.50 wt% based on the 3,4-diacetoxy-1-butene, an amine-exchange capacity corresponding to 0.02 wt% of triphenyl phosphine), followed by stirring at 30°C for 1 hour. As a result of the analysis of the liquid after the reaction, by gas chromatography, the weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 30:70. Further, dodecane was used as the internal standard material. The results are shown in Table 1.

COMPARATIVE EXAMPLE 2

The operation was carried out in the same manner as in Example 1, except that 38.9 mg of an anion-exchange resin (Diaion, WA20) was added instead of triphenyl

phosphine (2.5 wt% based on the 3,4-diacetoxy-1-butene, an amine-exchange capacity corresponding to 0.1 wt% of triphenyl phosphine), followed by stirring at 30°C for 1 hour. As a result of the analysis of the liquid after
5 the reaction, by gas chromatography, the weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 33:67. Further, dodecane was used as the internal standard material. The results are shown in Table 1.

10 COMPARATIVE EXAMPLE 3

To 3.0 cc of the 3,4-diacetoxy-1-butene-containing liquid obtained in the above Reference Example 3 "Purification and Distillation of 3,4-Diacetoxy-1-Butene-Containing Liquid" (the purified 3,4-diacetoxy-1-butene
15 comprising 72 wt% of the 3,4-diacetoxy-1-butene and 18 wt% of 3-hydroxy-4-acetoxy-1-butene, and additionally, 6 wt% of components having lower boiling points than the 3,4-diacetoxy-1-butene and 4 wt% of components having higher boiling points than the 3,4-diacetoxy-1-butene),
20 0.06 cc of acetic acid was added in the Schlenk flask and mixed, followed by heating to 130°C in an oil bath. 18 µL of the catalyst solution prepared in Reference Example 5 was added thereto, in the nitrogen atmosphere, followed by heating and stirring at 130°C for 3 hours (the
25 concentration of palladium in the reaction liquid was 1.0 wtppm). As a result of the analysis of the liquid after the isomerization reaction, by gas chromatography, the

weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 44:56. Further, dodecane was used as the internal standard material. The results are shown in Table 2.

5 COMPARATIVE EXAMPLE 4

To 3.0 cc of the 3,4-diacetoxy-1-butene-containing liquid obtained in the above Reference Example 3 "Purification and Distillation of 3,4-Diacetoxy-1-Butene-Containing Liquid" (the purified 3,4-diacetoxy-1-butene
10 comprising 72 wt% of the 3,4-diacetoxy-1-butene and 18 wt% of 3-hydroxy-4-acetoxy-1-butene, and additionally, 6 wt% of components having lower boiling points than the 3,4-diacetoxy-1-butene and 4 wt% of components having higher boiling points than the 3,4-diacetoxy-1-butene),
15 0.06 cc of acetic acid was added in the Schlenk flask and mixed, followed by heating to 130°C in an oil bath. 18 µL of the catalyst solution prepared in Reference Example 6 was added thereto, in the nitrogen atmosphere, followed by heating and stirring at 130°C for 3 hours (the
20 concentration of palladium in the reaction liquid was 1.0 wtppm). As a result of the analysis of the liquid after the isomerization reaction, by gas chromatography, the weight ratio of the 1,4-diacetoxy-2-butene (the total of cis and trans) to the 3,4-diacetoxy-1-butene was 40:60.
25 Further, dodecane was used as the internal standard material. The results are shown in Table 2.

TABLE 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Additive	Triphenyl phosphine	Triphenyl phosphine	Triphenyl phosphine	Triphenyl phosphine
Amount (mg) of additive	0.166	0.332	0.166	0.166
Amount (wt%) of additive based on 3,4-DABE (*1)	0.0073	0.0147	0.0073	0.0073
Contacting temperature (°C)	150	150	150	30
Contacting time	3 hours	3 hours	1 hour	5 minutes
Catalyst ligand for isomerization reaction	2,2'-Bis[bis(1-naphthoxy)phosphinyloxy]-3,3',5,5'-di-tert-butyl-6,6'-dimethyl-1,1'-biphenyl 	2,2'-Bis[bis(1-naphthoxy)phosphinyloxy]-3,3',5,5'-di-tert-butyl-6,6'-dimethyl-1,1'-biphenyl 	2,2'-Bis[bis(1-naphthoxy)phosphinyloxy]-3,3',5,5'-di-tert-butyl-6,6'-dimethyl-1,1'-biphenyl 	2,2'-Bis[bis(1-naphthoxy)phosphinyloxy]-3,3',5,5'-di-tert-butyl-6,6'-dimethyl-1,1'-biphenyl
Weight ratio of 1,4-DABE (*2) to 3,4-DABE, contained in reaction liquid after isomerization	45:55	44:56	45:55	40:60
Weight ratio (after isomerization) of 1,4-DABE to additive	4066	1988	4066	3614

(*1) 3,4-DABE: 3,4-diacetoxy-1-butene

(*2) 1,4-DABE: 1,4-diacetoxy-2-butene (the total of cis and trans)

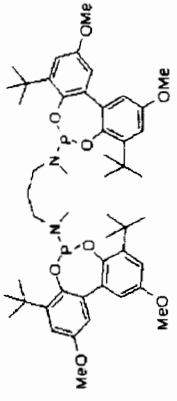
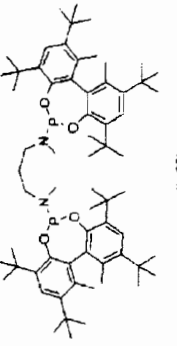
TABLE 1 (Continued)

	Ex. 5	Comp. Ex. 1	Comp. Ex. 2
Additive	Triphenyl phosphite	Anion-exchange resin	Anion-exchange resin
Amount (mg) of additive	0.166	7.8	38.9
Amount (wt%) of additive based on 3,4-DABE (*1)	0.0073	0.5	2.5
Contacting temperature (°C)	150	30°C	30°C
Contacting time	3 hours	1 hour	1 hour
Catalyst ligand for isomerization reaction	2,2'-Bis[bis(1-naphthoxy)-3,3',5,5'-di-tert-butyl-6,6'-dimethyl-1,1'-biphenyl]	2,2'-Bis[bis(1-naphthoxy)-3,3',5,5'-di-tert-butyl-6,6'-dimethyl-1,1'-biphenyl]	2,2'-Bis[bis(1-naphthoxy)-3,3',5,5'-di-tert-butyl-6,6'-dimethyl-1,1'-biphenyl]
Weight ratio of 1,4-DABE (*2) to 3,4-DABE, contained in reaction liquid after isomerization	36:62	30:70	33:67
Weight ratio (after isomerization) of 1,4-DABE to additive	3253	58	13

(*1) 3,4-DABE: 3,4-diacetoxy-1-butene

(*2) 1,4-DABE: 1,4-diacetoxy-2-butene (the total of cis and trans)

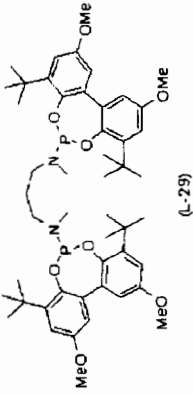
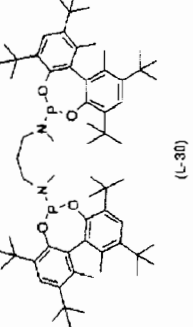
TABLE 2

	Ex. 6	Ex. 7
Additive	Triphenyl phosphine	Triphenyl phosphine
Amount (mg) of additive	0.15	0.15
Amount (wt%) of additive based on 3,4-DABE (*1)	0.005	0.005
Contacting temperature (°C)	150	150
Contacting time	3 hours	3 hours
Catalyst ligand for isomerization reaction	N1,N3-Dimethyl-N1,N3-bis[4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin-6-yl]-1,3-propanediamine  (L-25)	N1,N3-Dimethyl-N1,N3-bis[2,4,8,10-tetrakis(1,1-dimethylethyl)-1,11-dimethyldibenzo[d,f][1,3,2]dioxaphosphepin-6-yl]-1,3-propanediamine  (L-30)
Weight ratio of 1,4-DABE (*2) to 3,4-DABE, contained in reaction liquid after isomerization	49:53	52:48
Weight ratio (after isomerization) of 1,4-DABE to additive	8644	9173

(*1) 3,4-DABE: 3,4-diacetoxy-1-butene

(*2) 1,4-DABE: 1,4-diacetoxy-2-butene (the total of cis and trans)

TABLE 2 (Continued)

		Comp. Ex. 3	Comp. Ex. 4
Additive		-	-
Amount (mg) of additive		-	-
Amount (wt%) of additive based on 3,4-DABE (*1)		-	-
Contacting temperature (°C)		-	-
Contacting time		-	-
Catalyst ligand for isomerization reaction		N1,N3-Dimethyl-N1,N3-bis[4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin-6-yl]-1,3-propanediamine	N1,N3-Dimethyl-N1,N3-bis[2,4,8,10-tetrakis(1,1-dimethylethyl)-1,11-dimethyldibenzo[d,f][1,3,2]dioxaphosphepin-6-yl]-1,3-propanediamine
		 (L-29)	 (L-30)
Weight ratio of 1,4-DABE (*2) to 3,4-DABE, contained in reaction liquid after isomerization		44:56	40:60
Weight ratio (after isomerization) of 1,4-DABE to additive		-	-

(*1) 3,4-DABE: 3,4-diacetoxy-1-butene

(*2) 1,4-DABE: 1,4-diacetoxy-2-butene (the total of cis and trans)

From the above results, it is evident that with respect to the actual added amount of the additive or the exchange capacity of phosphorus and nitrogen atoms, the results of the isomerization reaction of Examples are improved as compared with Comparative Examples.

INDUSTRIAL APPLICABILITY

The present invention is an isomerization method of an allyl compound, which makes it possible to obtain an isomer with a high yield by using a small amount of a catalyst, and which is industrially useful.

The entire disclosure of Japanese Patent Application No. 2007-132184 filed on May 17, 2007 including specification, claims, drawings and summary is incorporated herein by reference in its entirety.

CLAIMS

1. An isomerization method comprising contacting a liquid containing an allyl compound as a raw material, with a phosphorus compound, and then, isomerizing the
5 above allyl compound in the presence of a catalyst.
2. The isomerization method according to Claim 1, wherein the above phosphorus compound is an organic phosphorus compound.
3. The isomerization method according to Claim 2,
10 wherein the above organic phosphorus compound is an organic phosphine.
4. The isomerization method according to Claim 3, wherein the above organic phosphine has at least two aryl groups.
- 15 5. The isomerization method according to Claim 3 or 4, wherein the above organic phosphine is triphenyl phosphine.
6. The isomerization method according to any one of Claims 1 to 5, wherein the amount of the phosphorus
20 compound which is contacted with the above allyl compound-containing liquid, is in a range of from 0.0001 to 10 weight%, based on the allyl compound.
7. The isomerization method according to any one of Claims 1 to 6, wherein the above allyl compound-
25 containing liquid and the phosphorus compound are contacted to each other at temperature of at least 60°C.
8. The isomerization method according to any one of

Claims 1 to 7, which further includes a step of obtaining the above allyl compound-containing liquid by diacetoxylation of a conjugated diene.

9. The isomerization method according to any one of
5 Claims 1 to 8, wherein the above catalyst is a liquid phase homogeneous palladium catalyst, which contains a phosphorus ligand having at least one P-O bond.

10. The isomerization method according to Claim 9,
wherein the above phosphorus ligand having a P-O bond, is
10 a bidentate phosphite.

11. The isomerization method according to Claim 9,
wherein the above phosphorus ligand having a P-O bond, is
a bidentate phosphoramidite.

12. A process for producing an allyl compound, which
15 comprises forming from an allyl compound the
corresponding isomerized allyl compound by using the
isomerization method as defined in any one of Claims 1 to
11.