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TITLE OF THE INVENTION

PROCESSES FOR PREPARING 4-tert.-BUTYLCYCLOHEXANOL
AND 4-tert.-BUTYLCYCLOHEXYL ACETATE

BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates to a process for preparing 4-tert.-butylcyclohexanol containing a larger amount of a cis-isomer by hydrogenating 4-tert.-butylphenol. The present invention also relates to a process for preparing 4-tert.-butylcyclohexyl acetate by acetylating 4-tert.-butylcyclohexanol obtained by the process described above.

Description of the Related Art

4-tert.-Butylcyclohexyl acetate is widely used as a perfume for cosmetics including soaps, and fragrance of its cis-isomer is more favorable than that of its trans-isomer. To prepare 4-tert.-butylcyclohexyl acetate having a high cis-isomer content, it is desired to provide a process for preparing 4-tert.-butylcyclohexanol containing its cis-isomer in a larger amount as a raw material of 4-tert.-butylcyclohexyl acetate.

In general, 4-tert.-butylcyclohexanol is prepared by hydrogenating 4-tert.-butylphenol.

JP-B-42-13938 discloses a process for preparing 4-tert.-butylcyclohexanol comprising catalytically reducing 4-tert.-butylphenol in the presence of a rhodium base catalyst.

MARUZEN OIL TECHNICAL REVIEW (MARUZEN SEKIYU GIHO) (1971) page 77 discloses a process for preparing 4-tert.-butylcyclohexanol comprising hydrogenating 4-tert.-butylphenol in the presence of various transition metals of the 8 to 10 Groups of the

Periodic Table.

JP-A-54-122253 discloses a process for preparing a cis alkylcyclohexanol comprising hydrogenating an alkylphenol in the presence of a ruthenium-alumina catalyst.

US-A-2927127 discloses a process for preparing 4-tert.-butylcyclohexanol which has a high cis-isomer content comprising hydrogenating 4-tert.-butylphenol.

JP-A-3-173842 discloses a process for preparing 4-tert.-butylcyclohexanol comprising hydrogenating 4-tert.-butylphenol in the presence of a combined catalyst of Rh supported on a carrier and a boron fluoride type acid such as HBF_4 .

However, the cis-isomer content in 4-tert.-butylcyclohexanol which is prepared by the processes disclosed in JP-B-42-13938, MARUZEN OIL TECHNICAL REVIEW and JP-A-54-122253 is still insufficient. The process of US-A-2927127 achieves a high cis-isomer content in ethanol in the presence of the rhodium catalyst, but the reaction should be performed under a high hydrogen pressure. Then, an improvement has been sought as a preparation process of 4-tert.-butylcyclohexanol. Further, since the process of JP-A-3-173842 uses the boron fluoride type acid, a workload is required to recover fluorine and boron, and the generated acids such as HF corrode a production equipment.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for preparing 4-tert.-butylcyclohexanol which can be carried out under a mild condition and produce 4-tert.-butylcyclohexanol having a high cis-isomer content.

Another object of the present invention is to provide a



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process for preparing 4-tert.-butylhexyl acetate having a high cis-isomer content.

According to the first aspect, the present invention provides a process for preparing 4-tert.-butylcyclohexanol comprising hydrogenating 4-tert.-butylphenol in a solvent in the presence of a rhodium catalyst and a compound selected from the group consisting of hydrogen chloride and (anhydrous) sulfuric acid.

According to the second aspect, the present invention provides a process for preparing 4-tert.-butylcyclohexyl acetate comprising acetylating 4-tert.-butylcyclohexanol which has been prepared by hydrogenating 4-tert.-butylphenol in a solvent in the presence of a rhodium catalyst and a compound selected from the group consisting of hydrogen chloride, perchloric acid and (anhydrous) sulfuric acid.

DETAILED DESCRIPTION OF THE INVENTION

The rhodium catalyst to be used in the hydrogenation reaction according to the present invention includes metal rhodium (valency of zero) or a compound of rhodium having a valency of up to 6 such as rhodium chloride, rhodium oxide and so on.

The metal rhodium or rhodium compound is preferably used in the form of a supported type catalyst, that is, the metal rhodium or rhodium compound supported on a carrier such as activated carbon, SiO_2 , Al_2O_3 , etc. Among the supported type catalyst, metal rhodium supported on the carrier is more preferable. In the case of the supported type catalyst, a supported amount of metal rhodium is usually between 1 and 10 wt. %, preferably between 3 and 5 wt. % based on the weight of the carrier.

After the reaction, the rhodium catalyst may be

recovered from a reaction mixture by a conventional method such as filtration, decantation, centrifugation, and recycled.

The amount of the rhodium catalyst to be used in the reaction is between about 0.01 and 1 wt. % (in terms of metal rhodium) based on the weight of the raw material, 4-tert.-butylphenol. In the case of the supported type catalyst, while an amount of the catalyst (including the carrier) depends on the supported amount of the rhodium metal or compound, it is between about 0.1 and 50 wt. % (in a dry form) based on the weight of 4-tert.-butylphenol. As the amount of the catalyst increases, the selectivity of the cis-isomer increases. The amount of the catalyst is preferably between 0.5 and 10 wt. % in view of the cost and workability in the filtration step for recovering the catalyst.

Any solvent may be used as long as it has no adverse effect on the reaction. A solvent which is liquid at room temperature (25°C) is preferable because of easy handling. Examples of the solvent are alkanes having 5 to 10 carbon atoms, ethers having 4 to 10 carbon atoms, alcohols having 1 to 6 carbon atoms, and so on. Specific examples of the solvent are acyclic alkanes (e.g. pentane, hexane, heptane, etc.), cyclic alkanes (e.g. cyclohexane, etc.), acyclic ethers (e.g. diethyl ether, etc.), cyclic ethers (e.g. tetrahydrofuran, dioxane, etc.), and alcohols (e.g. methanol, ethanol, propanol, isopropanol, butanol, isobutanol, pentanol, hexanol, 4-methyl-2-pentanol, cyclohexanol, etc.). Among them, cyclohexane and isopropanol are preferable. In particular, isopropanol is preferable.

The amount of the solvent is usually between about 0.2 and 20 times, preferably between 0.4 and 5 times the weight of 4-tert.-butylphenol.

In the process of the present invention, the reaction is performed in the solvent in the presence of the rhodium catalyst and also hydrogen chloride, perchloric acid or (anhydrous) sulfuric acid.

Hydrogen chloride may be supplied in the reaction system in any form, for example, by bubbling hydrogen chloride gas through the reaction system, or adding hydrochloric acid to the reaction system. Alternatively, hydrochloric acid may be formed in the reaction system, for example, by charging water and AlCl_3 or TiCl_4 to the reaction system. In addition, a catalyst which generates hydrogen chloride in the reaction system such as rhodium chloride may be used.

Also, (anhydrous) sulfuric acid may be supplied in the reaction system in any form, for example, by bubbling SO_3 gas through the reaction system or adding an aqueous sulfuric acid solution to the reaction system. Perchloric acid is added to the reaction system generally in the form of an aqueous solution.

An order of the addition of the raw material, the rhodium catalyst, the solvent and hydrogen chloride, perchloric acid or (anhydrous) sulfuric acid is arbitrary.

The amount of hydrogen chloride, perchloric acid or (anhydrous) sulfuric acid is usually between about 0.01 and 100 moles, preferably between about 0.05 and 10 moles, more preferably between 0.1 and 10 moles per one mole of the rhodium atom in the rhodium catalyst.

The process of the present invention may be carried out in a stream of hydrogen gas or in a pressurized hydrogen atmosphere. Other reaction conditions may not be critical. In view of a reaction rate, the reaction is preferably carried out in the pressu-

rized hydrogen atmosphere. In this case, a pressure reactor is used.

When the reaction is carried out under the pressurized hydrogen atmosphere, a partial pressure of hydrogen is at least about 1.5×10^5 Pa. In view of the reaction rate, the selectivity of the cis-isomer and the pressure resistance of the equipment, the partial pressure of hydrogen is preferably between 3×10^5 and 2×10^6 Pa, more preferably between 5×10^5 and 1.5×10^6 Pa.

The reaction temperature is at least about 20°C in view of the reaction rate and the selectivity of the cis-isomer, and preferably 100°C or lower in view of the selectivity of the cis-isomer. More preferably, the reaction temperature is between 40 and 80°C in view of the reaction rate and the selectivity of the cis-isomer.

The process of the present invention may be carried out continuously or batchwise.

The termination of the reaction can be confirmed by a conventional method. For example, the reaction mixture is analyzed and a time when the conversion of 4-tert.-butylphenol is 100 % is used as the termination of the reaction, or a time when no further decrease of the hydrogen pressure is observed is used as the termination of the reaction.

Furthermore, 4-tert.-butylcyclohexanol obtained by the above reaction can be acetylated to obtain 4-tert.-butylcyclohexyl acetate.

The acetylation can be performed continuously from the above hydrogenation of 4-tert.-butylphenol. Alternatively, 4-tert.-butylcyclohexanol obtained by the above reaction can be once isolated from the reaction mixture and then acetylated in a separate

step.

For acetylation, any conventional acetylation agent such as acetic anhydride, acetic acid, acetyl chloride, and the like may be used.

The amount of the acetylation agent is usually between 1 mole and 5 moles, preferably between 1 mole and 1.5 moles, per one mole of 4-tert.-butylcyclohexanol.

The reaction temperature in the acetylation is usually between room temperature (about 25°C) and 150°C, preferably between room temperature (about 25°C) and 130°C.

The acetylation can be terminated when the conversion of 4-tert.-butylcyclohexanol is found to be 100 % through the analysis of the reaction mixture.

The presence of a solvent is not essential in the acetylation process, while a solvent which is less acetylated may be used. Solvents which are in the liquid state at room temperature is preferable in view of easy handling. Examples of such the solvent are acyclic alkanes (e.g. pentane, hexane, heptane, etc.), cyclic alkanes (e.g. cyclohexane, etc.), unsaturated hydrocarbons (e.g. toluene, etc.), acyclic ethers (e.g. diethyl ether, etc.), cyclic ethers (e.g. tetrahydrofuran, etc.), and the like. Among them, toluene and cyclohexane are preferable.

In addition to the acetylation agent, a catalyst may be used in the acetylation reaction. The kind of the catalyst depends on the acetylation agent to be used. For example, sulfuric acid, hydrochloric acid, p-toluenesulfonic acid, zinc chloride, sodium acetate, pyridine, and the like can be used, when acetic anhydride is used as the acetylation agent. Alternatively, sulfuric acid or BF_3



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may be used, when acetic acid is used as the acetylation agent.

Among these catalyst, sulfuric acid is preferably in view of a cost.

The amount of the catalyst is usually between 0.01 and 5 mole %, preferably between 0.1 and 2 mole %, of the amount of 4-tert.-butylcyclohexanol. When the amount of the catalyst is too small, the reaction rate is too low, while it is too larger 4-tert.-butylhexanol tends to be dehydrated.

When acetic acid is used as the acetylation agent, the acetylation is preferably carried out while removing by-produced water in view of the reaction rate. Water may be removed by evaporating water azeotropically with a solvent which can be evaporated azeotropically with water under refluxing conditions, or by adding a drying agent such as silica gel to the reaction system.

When acetyl chloride is used as the acetylation agent, the acetylation is preferably carried out while removing by-produced hydrogen chloride in view of safety. Hydrogen chloride may be removed with a base such as inorganic bases (e.g. potassium carbonate, 10 % sodium hydroxide, etc.) or organic bases (e.g. pyridine, etc.) potassium carbonate.

Among the acetylating agents, acetic anhydride is preferable in view of the conversion of the raw material in the acetylation reaction.

It is difficult to separate resulting 4-tert.-butylcyclohexyl acetate from 4-tert.-butylcyclohexanol by distillation since they have the close boiling points. Therefore, the conversion of 4-tert.-butylhexanol is preferably equal or close to 100 %. To this end, for example, acetic acid or acetyl chloride is used as the acetylation agent and the acetylation reaction is carried out until

the conversion reaches about 90 % or higher, and then the acetylation is completed with acetic anhydride in the same molar amount as the residual raw material so that the raw material is consumed completely.

EFFECTS OF THE INVENTION

The process of the present invention can easily prepare 4-tert.-butylcyclohexanol having the high content of the cis-isomer useful as a raw material of a perfume from 4-tert.-butylphenol. That is, 4-tert.-butylcyclohexanol can be obtained at a yield of about 90 % or higher, and the content of the cis-isomer in the product reaches about 80 % or more.

4-tert.-Butylcyclohexyl acetate having the high content of the cis-isomer can be obtained by acetylating 4-tert.-butylhexanol which has been prepared by the process of the present invention.

EXAMPLES

The present invention will be illustrated by the following Examples, which do not limit the present invention in any way.

Example 1

4-tert.-Butylphenol (90 g, 0.60 mole), 5 %Rh/C (namely 5 wt. % of rhodium metal supported on a activated carbon carrier) (1.35 g based on the dry material), isopropanol (180 g) and 36 % hydrochloric acid (0.18 g) were charged into an autoclave, and then the interior of the autoclave was replaced with nitrogen gas by injecting the nitrogen gas up to 5×10^5 Pa and evacuating it three times. After replacing the interior of the autoclave with hydrogen by injecting the hydrogen gas up to 5×10^5 Pa and evacuating it three times, the hydrogen gas was injected up to 1.1×10^6 Pa, and an interior temperature was raised to 60°C, followed by stirring for

1.75 hours.

After cooling the autoclave and replacing the interior with the nitrogen gas in the same way as above, the reaction mixture was analyzed. The yield of 4-tert.-butylcyclohexanol was 93.4 %, and the ratio of the cis-isomer to trans-isomer was 89.9:10.1.

Examples 2-10

4-tert.-Butylcyclohexanol was prepared in the same manner as in Example 1 except that the reaction conditions were changed as shown in the Table. In Example 10, 98 % sulfuric acid was used.

The results are shown in the Table.

In all of Examples 1-10, the conversion of 4-tert.-butylphenol was 100 %.

Comparative Examples 1-3

4-tert.-butylcyclohexanol was prepared in the same manner as in Example 1 except that no acid was used (Comparative Example 1), phosphoric acid (85 %) was used (Comparative Example 2) or nitric acid (61 %) was used (Comparative Example 3).

The results are shown in the Table.

Comparative Examples 4 and 5

4-tert.-butylcyclohexanol was prepared in the same manner as in Example 1 except that a Ru catalyst (5 %Ru/C) was used (Comparative Examples 4 and 5) and no hydrochloric acid was used (Comparative Example 5).

The results are shown in the Table.

In Comparative Example 4, the conversion of 4-tert.-butylphenol was 42.2 %, while in other Comparative Examples, the

Table

Ex. No.	Catalyst		Acid		Solvent		Hydrogen partial pressure x 10 ⁵ Pa	Temp. (°C)	Time (hr.)	BCHL	
	Kind	Amount (g)	Kind	Amount (g)	Kind	Amount (g)				Yield (%)	Cis/trans ratio
1	Rh	1.35	Hydro-chloric acid	0.18	IPA	180	11	60	1.75	93.4	89.9/10.1
2	↑	0.90	↑	0.12	↑	↑	↑	↑	3.0	93.4	87.8/12.2
3	↑	2.25	↑	0.30	↑	74	21	40	5.0	93.0	86.3/13.7
4	↑	1.45	↑	0.18	CHX	180	11	60	1.2	96.3	86.3/13.7
5	↑	2.25	↑	0.30	↑	360	6	40	0.6	96.0	87.6/12.4
6	↑	↑	↑	↑	↑	74	41	↑	0.3	96.1	86.6/13.4
7	↑	↑	↑	↑	↑	↑	21	80	0.5	96.6	84.1/15.9
8	↑	↑	↑	0.60	↑	↑	↑	40	1.0	94.6	89.8/10.2
9	↑	4.50	↑	↑	↑	↑	↑	↑	0.5	95.9	91.2/8.8
10	↑	2.19	Sulfuric acid	0.15	↑	↑	↑	↑	↑	97.0	78.9/20.1

conversion of 4-tert.-butylphenol was 100 %.

Table (cont'd)

Ex. No.	Catalyst		Acid		Solvent		Hydrogen partial pressure x 10 ⁵ Pa	Temp. (°C)	Time (hr.)	BCHL	
	Kind	Amount (g)	Kind	Amount (g)	Kind	Amount (g)				Yield (%)	Cis/trans ratio
C. 1	Rh	4.50	None	---	CHX	74	21	40	0.3	96.6	68.5/31.5
C. 2	↑	2.25	Phosphoric acid	0.23	↑	↑	↑	↑	0.7	97.0	68.6/31.4
C. 3	↑	2.19	Nitric acid	0.31	↑	↑	↑	↑	7.0	69.9	60.7/39.3
C. 4	Ru	4.50	Hydrochloric acid	0.30	↑	↑	↑	↑	10.0	39.8	68.3/31.7
C. 5	↑	↑	None	---	↑	↑	↑	↑	1.5	97.8	63.2/36.8

Notes: IPA: Isopropanol.

CHX: Cyclohexane.

BCHL: 4-tert.-Butylcyclohexanol.

Example 11

(1) 4-tert.-Butylphenol (90 g, 0.60 mole), 5 %Rh/C (0.9 g based on the dry material), isopropanol (180 g) and a 60 % aqueous solution of perchloric acid (0.10 g) were charged into an autoclave, and then the interior of the autoclave was replaced with nitrogen gas by injecting the nitrogen gas up to 5×10^5 Pa and evacuating it three times. Hydrogen gas was injected up to 1.1×10^6 Pa, and an interior temperature was raised to 60°C, followed by stirring for 5 hours.

After cooling the autoclave and replacing the interior with the nitrogen gas in the same way as above, the reaction mixture was analyzed. The yield of 4-tert.-butylcyclohexanol was 95.5 %, and the ratio of the cis-isomer to trans-isomer was 82.1:17.9.

The reaction mixture was filtrated to remove the catalyst, and evaporated for concentration to obtain crude 4-tert.-butylcyclohexanol (91 g, 0.57 mole, a purity of 98.4 %, the ratio of the cis-isomer to trans-isomer being 82.1:17.9).

(2) Sulfuric acid (0.17 g, 1.8 mmoles) was added to the above concentrated mixture while maintaining the mixture at 90°C, and then acetic anhydride (76.06 g, 0.75 mole) was dropwise added to the mixture over 3 hours, followed by keeping that temperature for 1 hour.

The analysis of the reaction mixture revealed that the yield of 4-tert.-butylcyclohexyl acetate was 99 % (based on 4-tert.-butylcyclohexanol), and the ratio of the cis-isomer to trans-isomer was 82.1:17.9.

The reaction mixture was washed with 5 % aqueous

sodium bicarbonate (each 120 g) three times, and with ion exchanged water (120 g) once. An oil layer was rectified, and 4-tert.-butylcyclohexyl acetate having high purity was obtained at a high yield.

Example 12

(1) 4-tert.-Butylphenol (180 g, 1.20 moles), 5 %Rh/C (1.8 g based on the dry material), isopropanol (360 g) and 36 % hydrochloric acid (0.12 g) were charged into an autoclave, and then the interior of the autoclave was replaced with nitrogen gas by injecting the nitrogen gas up to 5×10^5 Pa and evacuating it three times. After replacing the interior of the autoclave with hydrogen by injecting the hydrogen gas up to 5×10^5 Pa and evacuating it three times, the hydrogen gas was injected up to 1.1×10^6 Pa, and an interior temperature was raised to 60°C, followed by stirring for 4 hours.

After cooling the autoclave and replacing the interior with the nitrogen gas in the same way as above, the reaction mixture was analyzed. The yield of 4-tert.-butylcyclohexanol was 93.2 %, and the ratio of the cis-isomer to trans-isomer was 88.6:11.4.

The above reaction was repeated, and the two reaction mixtures were combined.

The combined reaction mixture was filtrated to remove the catalyst, and evaporated for concentration to obtain crude 4-tert.-butylcyclohexanol (350 g, 2.20 mole, a purity of 98.4 %, the ratio of the cis-isomer to trans-isomer being 88.6:11.4).

(2) Sulfuric acid (0.81 g, 8.1 mmoles) was added to the above concentrated mixture while maintaining the mixture at 90°C,

and then acetic anhydride (312.4 g, 2.94 moles) was dropwise added to the mixture over 3 hours, followed by keeping that temperature for 1 hour.

The analysis of the reaction mixture revealed that the yield of 4-tert.-butylcyclohexyl acetate was 99 % (based on 4-tert.-butylcyclohexanol), and the ratio of the cis-isomer to trans-isomer was 88.6:11.4.

The reaction mixture was washed with 5 % aqueous sodium bicarbonate (each 450 g) three times, and with ion exchanged water (450 g) once. An oil layer was rectified, and 4-tert.-butylcyclohexyl acetate having high purity was obtained at a high yield.



What is claimed is:

1. A process for preparing 4-tert.-butylcyclohexanol comprising hydrogenating 4-tert.-butylphenol in a solvent in the presence of a rhodium catalyst and a compound selected from the group consisting of hydrogen chloride, perchloric acid and (anhydrous) sulfuric acid.
2. The process according to claim 1, wherein an amount of hydrogen chloride, perchloric acid or (anhydrous) sulfuric acid is from 0.05 to 10 moles per one mole of the rhodium atom in the rhodium catalyst.
3. The process according to claim 1, wherein said rhodium catalyst comprises metal rhodium supported on a carrier.
4. The process according to claim 3, wherein an amount of the rhodium catalyst (in terms of the dry material) is from 0.5 to 10 wt. % based on the weight of 4-tert.-butylphenol.
5. The process according to claim 1, wherein said solvent is a solvent selected from the group consisting of alkanes having 5 to 10 carbon atoms, ethers having 4 to 10 carbon atoms and alcohols having 1 to 6 carbon atoms.
6. The process according to claim 5, wherein said solvent is an alcohol.
7. The process according to claim 6, wherein said alcohol is isopropanol.
8. The process according to claim 1, wherein a reaction temperature is from 20 to 100°C.
9. A process for preparing 4-tert.-butylcyclohexyl acetate comprising acetylating 4-tert.-butylcyclohexanol which has been prepared by hydrogenating 4-tert.-butylphenol in a solvent in



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the presence of a rhodium catalyst and a compound selected from the group consisting of hydrogen chloride, perchloric acid and (anhydrous) sulfuric acid.