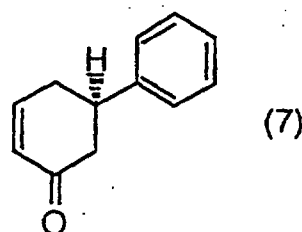
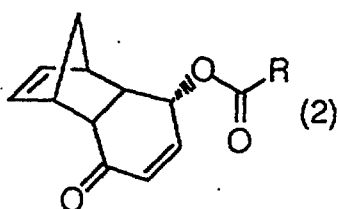


CYCLOHEXENE AND CYCLOHEXENONE DERIVATIVES AND PROCESS FOR
PRODUCTION OF CYCLOHEXENE DERIVATIVES

The present invention relates to optically active
5 cyclohexene derivatives, processes of production of
optically active cyclohexenone derivatives, which include
compounds represented by the following formulae, useful as
a starting material for synthesizing natural products, and
intermediates used for the above production.

10



15 The optically active cyclohexenone derivative repre-
sented by the formula (7) is a very useful compound as an
intermediate for synthesizing natural materials (for
example, "Total Synthesis of Natural Products", ApSimon
edit, vol. 2, 1973 and vol. 5, 1983, and J. d'Angelo,
20 Tetrahedron, 32, 2979 (1976)). Takei et al. synthesized
an optically active cyclohexenone derivative (7) by using
optically active 5-trimethylsilylcyclohexene-2-one as a
starting material (J. Chem. Soc., Chem. Commun., 1988,
430).

25 However, optically active 5-trimethylsilylcyclohex-
ene-2-one is obtained by repeated recrystallization of a
diastereomer salt synthesized from a racemate of the
starting material with cinchonidine and toluenethiol.
The method is not for practical use because it has many
30 steps and a low yield of 3% (Tetrahedron, Lett., 28,
5669 (1987)).

The optically active cyclohexenone derivative repre-
sented by the formula (2) is a starting material for
synthesizing eutypoxide B, a metabolite of the fungus
35 Eurypa lata. The racemic total synthesis of eutypoxide B

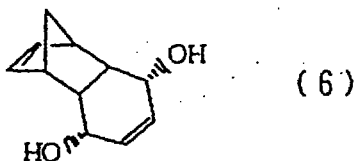


has been reported by Tabacchi and co-workers and employs a Diels-Alder reaction as the key step (Helv. Chim. Acta, 75, 276 (1992)). However, the key reaction directed diasterofacial selection incorrectly to furnish the diastereomeric mixture containing the desired epimer only in a ratio which could be fortuitously separated in a later stage.

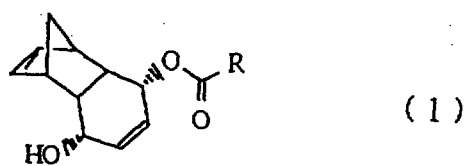
Thus, prior to the present invention, there is no efficient method for producing optically active cyclohexenone derivatives.

Considering the above, the inventors of the present invention have earnestly studied to attain this object and to efficiently obtain optically active cyclohexenone derivatives having high purity as intermediates for synthesizing natural compounds, so that they have found optically active cyclohexene derivatives useful as intermediates and the optically active cyclohexenone derivatives, and the method for producing efficiently the compounds has been established.

The present invention can provide a process in which an optically active cyclohexenone derivative is obtained by a process comprising using as a starting material a cyclohexene diol represented by the formula:

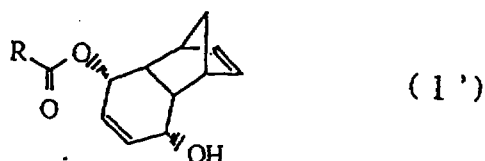


reacting the cyclohexene diol with an ester in the presence of lipase by transesterification selectively in a position to obtain an optically active cyclohexene derivative represented by the general formula:



5

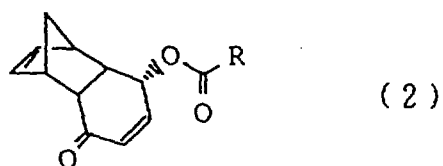
or



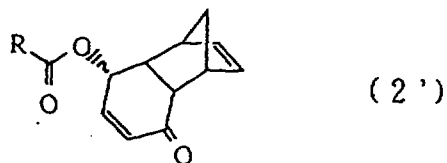
10

wherein R is alkyl, then oxidizing the hydroxy group of the derivative to obtain an optically active cyclohexenone derivative represented by the formula:

15



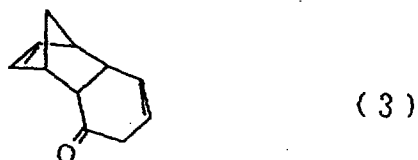
20 or



25

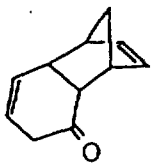
wherein R is alkyl, and reacting the resultant derivative by deacyloxylation to obtain an optically active cyclohexenone derivative represented by the formula:

30



or

35

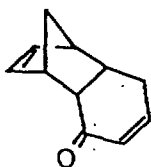


(3')

5

Then, the last compound is isomerized to obtain an optically active cyclohexenone derivative represented by the formula:

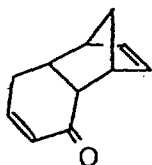
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(4)

or

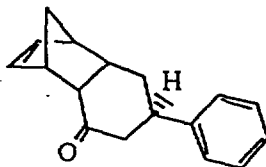
15



(4')

20 reacting the resultant compound with a Grignard reagent to obtain an optically active derivative represented by the formula:

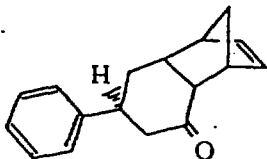
25



(5)

or

30

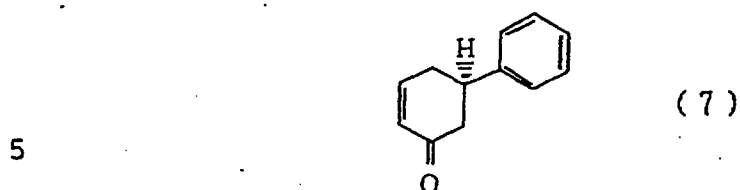


(5')

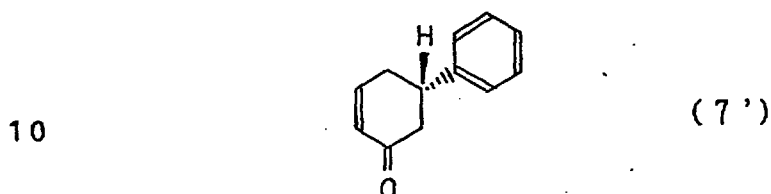
and reacting the resultant compound by a retro Diels-Alder reaction to obtain an optically active cyclohexe-

35

none derivative represented by the formula:

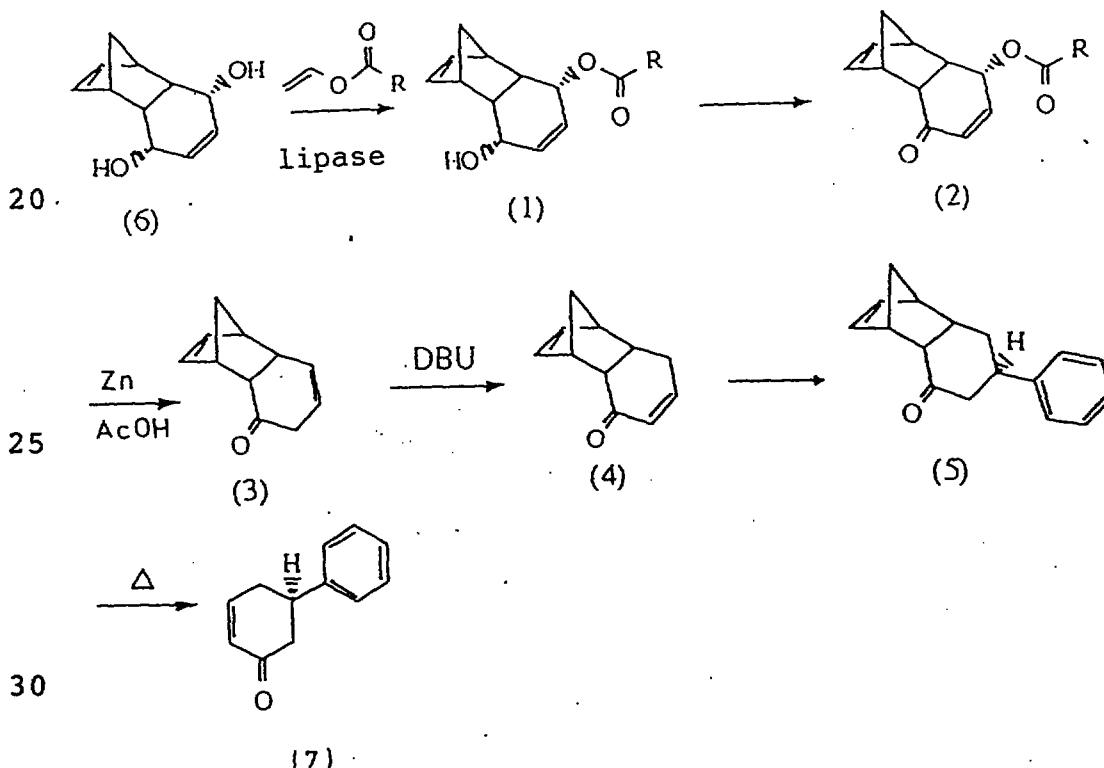


or



The reaction steps of the process of the present invention are exemplified in the following:

15



The cyclohexene diol derivative (6) of the starting material in the present invention can easily be obtained by reduction of a carbonyl group of a cyclohexenone derivative, which

35

can be obtained by a common Diels-Alder reaction of cyclopentadiene and hydroquinone, in the presence of a reducing agent such as lithium aluminum hydride.

5 The resultant hexenediol derivative (6) may be reacted by transesterification with a specified ester in the presence of lipase. Otherwise, the derivative (6) may be reacted by a conventional method and the diacetate obtained hydrolyzed in the presence of lipase. Then, the optically active cyclohexene
10 derivative (1) or (1') of the present invention can be obtained. In the case of the transesterification reaction, fatty acid vinyl esters, triglycerides, acid anhydrides and several kinds of esters are examples of the specified ester. Fatty acid vinyl esters are
15 preferably used. Any lipase having a catalytic effect in the reaction can be used. In particular, commercially available lipase PS (manufactured by Amano Pharmaceutical Co., Ltd.) derived from a Pseudomonas genus is preferred. Any solvent by which the reaction
20 is not inhibited can be used, or the reaction can be conducted in the presence of the substrate alone and without solvent. Preferably, acetonitrile is used as a reaction solvent.

25 When the cyclohexene derivative (1) is reacted with an oxidising agent such as manganese dioxide by a common oxidation reaction, a hydroxyl group is changed into a carbonyl group to obtain the cyclohexene derivative represented by the formula (2).

30 Then the resultant derivative can be treated with ultrasonic waves in the presence of zinc to deacyloxylate by a common method, and the cyclohexenone derivative represented by the formula (3) obtained.

35 Further, the resultant compounds is isomerized by any method to obtain the cyclohexenone derivative represented by the formula (4).



The compound (4) may be reacted with a Grignard reagent such as phenyl magnesium bromide by a nucleophilic reaction (Takei et al., Tetrahedron Lett., 28, 5669 (1987)), and the cyclohexenone derivative represented by the formula (5) obtained.

The compound can be changed into the optically active cyclohexenone derivative represented by the formula (7) useful as an intermediate of natural compounds by a general retro Diels-Alder reaction.

The alkyl groups R and R' and preferably C₁ to C₃₅ alkyl groups, more preferably C₁ to C₂₂ alkyl groups.

The present invention can provide the following merits.

1. Optically active cyclohexene derivatives useful for natural material synthesis, which are represented by the above formulas (1) or (1') - (4) or (4') and (7) or (7'), are obtained efficiently and the derivatives have high purity.

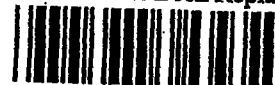
2. Each intermediate represented by the above formulas (1) or (1') - (5) or (5') and (7) or (7') can be changed into useful chiral elements.

3. The cyclohexene derivative represented by the above formula (1) or (1') is a meso compound, so that it acts as two antipodes by distinction between a hydroxy group and an acyloxy group. Accordingly, the compound (1) or (1') can be prepared from the same compound (6), and the compound (2) or (2') and the like can be prepared similarly.

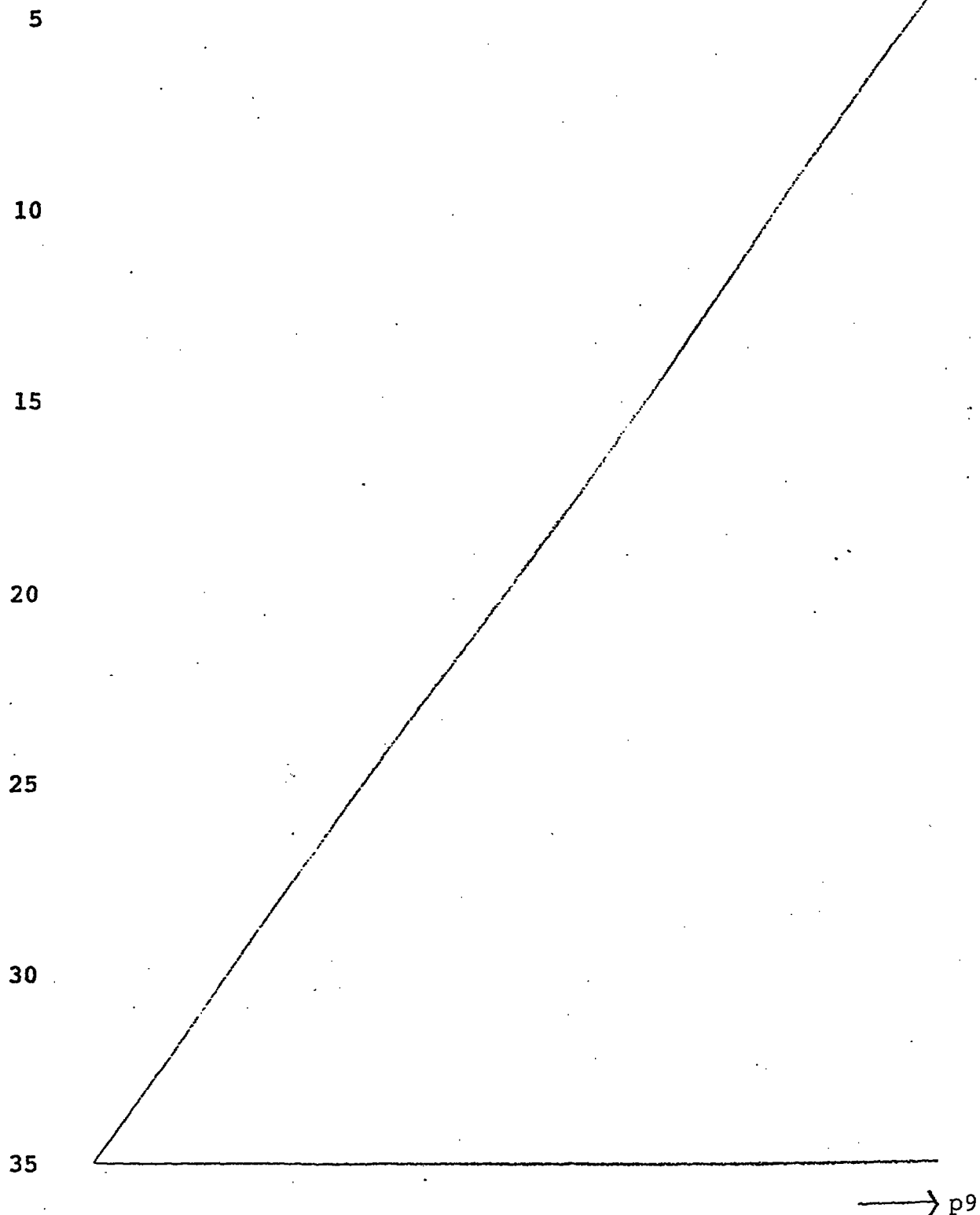
The following examples illustrate this invention more specifically, but these will not always be precise in practical applications.

Example 1

To an acetonitrile solution of a hexenediol derivative (6) (100 mg, 0.56 mmol) and vinyl acetate (0.3 ml, 3.36 mmol), lipase PS (100 mg) was suspended,



and the mixture was stirred for two weeks at room temperature. After the lipase was filtered away, the filtrate was concentrated under reduced pressure, and the residue was



purified with a chromatograph over silica gel to obtain a diacetate (5 mg, 3.4%), a monoacetate (1) (101 mg, 89%) and 15 mg of unreacted materials. The specific rotation of the monoacetate was $[\alpha]_D^{29} 63.1^\circ$ (c2.20, CHCl_3).

5 Further, the other values of physical properties were as follows:

IR (neat) 1737 cm^{-1}

$^1\text{H-NMR}$ (90 MHz), CDCl_3

1.20-1.40(m, 2H), 1.73-2.25(br, 1H), 2.08(s, 3H),
10 2.71-3.18(m, 4H), 4.39-4.48(m, 1H), 5.19-5.57(m, 3H),
5.74-5.93(m, 2H).

Example 2

A dichloromethane solution (5 ml) of the monoacetate (1) (600.3 mg, 2.72 mmol) was added dropwise in a suspended dichloromethane solution (10 ml) of manganese dioxide (3.56 g, 40.9 mmol) on ice cooling, and the mixture was stirred for 30 minutes at the same temperature. Unreacted materials were filtered off, the filtrate was concentrated under reduced pressure, and the residue was chromatographed over silica gel to obtain a ketone (2) (491 mg, 82%). The specific rotation was $[\alpha]_D^{29} -219.9^\circ$ (c1.29, CHCl_3). Further, the value of elemental analysis was as follows:

Calculated C:71.54, H:6.47

25 Found C:71.43, H:6.47

The other values of physical properties were as follows:

IR (neat) $1741, 1669 \text{ cm}^{-1}$

$^1\text{H-NMR}$ (90 MHz), CDCl_3

1.23-1.51(m, 2H), 2.17(s, 3H), 2.89-3.48(m, 4H),
30 5.60-5.93(m, 3H), 6.11(dd, 1H, $J=5.4\text{Hz}, 2.7\text{Hz}$),
6.45(ddd, 1H, $J=10.2, 2.4, 1.0\text{Hz}$)

Example 3

To a mixed solution of the ketone (2) (97 mg, 0.44 mmol) in ethanol-acetic acid (2.1 ml-0.7 ml), 150 mg of



zinc powder was suspended, and the mixture was irradiated with ultrasonic wave at room temperature for 3.5 hours. Insoluble materials were filtered off, the filtrate was concentrated under reduced pressure, and the residue was
5 extracted with ether. The ether layer was washed with 5% aqueous solution of sodium bicarbonate and with water, and then the layer was dried over magnesium sulfate. The solvent was distilled away under reduced pressure, and the residue was chromatographed over silica gel to obtain
10 the compound represented by the formula (3) (42 mg, 43%). The values of physical properties were as follows:

IR (neat) 1701 cm^{-1}

$^1\text{H-NMR}$ (90 MHz), CDCl_3

1.31-1.55(m, 2H), 2.31-2.74(m, 2H), 2.80-3.22(m, 3H),
15 2.80-3.22(m, 3H), 3.28-3.46(m, 1H), 5.43-5.64(m, 1H),
5.72-5.89(m, 1H), 5.98-6.28(m, 2H)

Example 4

A β , γ -unsaturated ketone (3) (42 mg, 0.26 mmol) and DBU (0.04 ml, 0.26 mmol) were dissolved in benzene (2
20 ml), and the mixture was stirred overnight at room temperature. Benzene was distilled away under reduced pressure, the residue was chromatographed over silica gel, and a α , κ -unsaturated ketone (4) (10 mg, 24%) was obtained. The values of physical properties were as
25 follows:

IR (neat) 1662 cm^{-1}

$^1\text{H-NMR}$ (90 MHz), CDCl_3

1.24-1.52(m, 2H), 1.84-2.26(m, 1H), 2.39-3.10(m, 4H),
3.30-3.48(m, 1H), 5.78-5.97(m, 1H), 6.04-6.23(m, 2H),
30 6.57-6.79(m, 1H)

Example 5

A α , β -unsaturated ketone (4) (10 mg, 24%) was dissolved in 10 ml of THF. To the solution, phenyl magnesium bromide (0.075 mmol, 10 ml of a THF solution) previously prepared was added dropwise on ice cooling. After
35

This Sheet Has Been Replaced



stirring for four hours, the reaction mixture was injected into a saturated solution of ammonium chloride on ice cooling. After the mixture was extracted with ether, the ether layer was washed with saturated sodium chloride solution. The ether layer was dried over magnesium sulfate, then ether was distilled away under reduced pressure, and the residue was obtained. The residue was purified by silica gel chromatography to obtain an optically active cyclohexanone derivative (5) (9 mg, 62%). Further, the compound in 1 ml of a diphenyl ether solution was heated and refluxed for 1.5 hours. The mixture solution was chromatographed over silica gel to obtain an optically active cyclohexenone derivative represented by the formula (6) (2.5 mg, 90%). The specific rotation was $[\alpha]_D^{31} -47.9^\circ$ (c0.52, CHCl_3), (a literature value ; $[\alpha]_D^{23} -46.4^\circ$ (c5.0, CHCl_3), and the result fits in with the literature value.

Example 6 Synthesis of eutypoxide B

(Application example)

Step 1

Vinyl magnesium bromide (2.1 ml, 1M THF sol.) was added to 4 ml of a THF solution of copper (I) bromide-dimethyl sulfide complex (7 mg, 0.03 mmol) and HMPA (0.25 ml, 1.4 mmol) at -78°C and the mixture was stirred for 10 minutes. A mixture of the enone (153 mg, 0.70 mmol) obtained by Example 5 and trimethylsilyl chloride (0.36 ml, 2.84 mmol) dissolved in 2 ml of THF was added dropwise to the above mixture and stirred for one hour at -78°C . Then, 3 ml of 5% hydrochloric acid was added. After rising to room temperature the mixture was stirred for 30 minutes. The reaction solution was diluted with ether, and washed with water, with saturated sodium bicarbonate solution and then with saturated sodium chloride solution. The ether layer was dried over magnesium sulfate, then ether was distilled away under reduced pressure, and



the residue was obtained. The residue was purified by silica gel chromatography to obtain a ketone (140 mg, 81%) of colorless crystals.

5 m.p. 73-74°C

$[\alpha]_D^{32} +20.9^\circ$ (c 0.94, CHCl_3)

IR (nujol) 1723, 1687 cm^{-1}

$^1\text{H-NMR}$ (300 MHz), CDCl_3 ; 1.29(br. d, $J=8.4$ Hz, 1H),

1.41(br. d, $J=8.6$ Hz, 1H), 2.11(s, 3H), 2.11-2.33(m, 2H),

10 2.53-2.61(m, 1H), 2.90-2.96(m, 2H), 3.05-3.12(m, 1H),

3.38(br. s, 1H), 4.98-5.07(m, 2H), 5.18(dd, $J=10.7$, 8.1

Hz, 1H), 5.60(ddd, $J=17.2$, 10.6, 6.3 Hz, 1H), 6.14-

6.21(m, 2H)

MS m/e 246(M^+), 66(100%)

15 HRMS calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$ 246.1256, Found 246.1253

Anal. calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$: C 73.15; H 7.37 Found C 73.14; H 7.34.

Step 2

Sodium borohydride (94 mg, 2.5 mmol) was added to 3
20 ml of a methanol solution of the ketone (305 mg, 1.24 mmol) obtained by Step 1 on ice cooling, and the mixture was stirred at the same temperature for 30 minutes. After rising to room temperature, potassium carbonate (300 mg, 2.17 mmol) was added, and the mixture was
25 stirred for 12 hours. The mixture was diluted with dichloromethane and washed with saturated sodium chloride solution. The dichloromethane layer was dried over magnesium sulfate, then the organic solvent was distilled away under reduced pressure, and the residue was chromat-
30 ographed over silica gel to obtain a diol (235 mg, 92%).

m.p. 132-133°C

$[\alpha]_D^{27} +72.2^\circ$ (c 1.16, MeOH)

IR (nujol) 3235 cm^{-1}

35 $^1\text{H-NMR}$ (300 MHz), CDCl_3 ; 1.33(d, $J=8.1$ Hz, 1H), 1.45-

1.54(m, 2H), 1.85(ddd, J=14.7, 10.2, 7.3Hz, 1H), 2.01(br.
d. J=5.1Hz, 1H), 2.30-2.36(m, 1H), 2.45-2.54(m, 2H),
2.62(ddd, J=11.0, 5.1, 3.3Hz, 1H), 2.94-2.98(m, 1H),
3.76-3.82(m, 1H), 4.14-4.18(m, 1H), 5.00-5.06(m, 2H),
5 5.71(ddd, J=16.9, 9.9, 8.4 Hz, 1H), 6.18-6.25(m, 2H)

MS m/e 206(M⁺), 66(100%)

HRMS calcd for C₁₃H₁₈O₂ 206.1307, Found 206.1313

Anal. calcd for C₁₃H₁₈O₂: C 75.69; H 8.8; Found C 75.69;
H 8.8.

10 Step 3

Four ml of a diphenyl ether solution of the diol (100
mg, 0.49 mmol) obtained by Step 2 was refluxed for 45
minutes. The reaction solution was chromatographed over
silica gel to obtain a retro D-A product (50 mg, 73%).

15

[α]_D³⁰ -33.2° (c 0.43, MeOH)

IR (film) 3328 cm⁻¹

¹H-NMR (300 MHz), CDCl₃; 1.57(ddd, J=14.3, 12.1, 4.4 Hz,
1H), 1.72(dt, J=13.5, 3.0 Hz, 1H), 2.26-2.37(m, 1H),
20 3.71(d, J=8.5 Hz, 1H), 4.01-4.04(m, 1H), 4.93-5.08(m,
2H), 5.69(br. s, 2H), 5.79(ddd, J=14.5, 10.6, 7.3 Hz, 1H)

MS m/e 122(M⁺-18), 86(100%)

HRMS calcd for C₈H₁₀O 122.0732, Found 122.0725

Step 4

25 Imidazole (50 mg, 0.73 mmol) and t-butyldimethylsilyl
chloride (81 mg, 0.54 mmol) were added to 0.5 ml of a DMF
solution of retro D-A product (25 mg, 0.18 mmol) on ice
cooling, and the mixture was stirred for four hours at room
temperature. Ether was added to the reaction solution,
30 and the solution was washed with saturated sodium chlo-
ride and dried over magnesium sulfate. The solvent was
distilled away under reduced pressure, and the residue
was chromatographed over silica gel to obtain t-butyl-
dimethylsilyl ether (62 mg, 94%).

35

$[\alpha]_D^{26} -9.6^\circ$ (c 1.03, CHCl_3)

IR (film) 1642 cm^{-1}

$^1\text{H-NMR}$ (90 MHz), CDCl_3 ; 0.06(s, 12H), 0.90(s, 18H),
1.42-1.91(m, 2H), 2.34-2.58(m, 1H), 3.86(d, $J=8.0\text{ Hz}$,
5 1H), 4.10-4.22(m, 1H), 4.95-5.19(m, 2H), 5.65(d, $J=1.2$
Hz, 2H), 5.65-6.12(m, 1H)

MS m/e 368(M^+), 147(100%)

HRMS calcd for $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}_2$ 314.2097 (M^+-54),

Found 314.2110

10 Step 5

m-Chloroperbenzoic acid (205 mg, 0.83 mmol) and
4,4'-Thiobis (6-tert-butyl-m-cresol)(10 mg, 0.028 mmol)
were added to 5 ml of a dichloroethane solution of t-
butyldimethylsilyl ether (102 mg, 0.28 mmol), and the
15 mixture was refluxed for 5 minutes. The mixture was
diluted with dichloromethane, and washed with saturated
sodium bicarbonate solution and then with saturated
sodium chloride solution. The organic layer was dried
over magnesium sulfate, and the solvent was distilled
20 away under reduced pressure. The residue was chromato-
graphed over silica gel to obtain a diepoxide (82 mg,
74%).

$^1\text{H-NMR}$ (90 MHz), CDCl_3 ; 0.10(s, 8H), 0.17(s, 4H), 0.90,
25 0.93, 0.94(3s, 18H), 1.15-1.68(m, 3H), 2.35-2.79 (m, 3H),
3.07(br. s, 2H) 3.73(d, $J=8.6\text{ Hz}$, 1H), 4.18-4.29(m, 1H)

MS m/e 343(M^+-^tBu), 147(100%)

HRMS calcd for $\text{C}_{16}\text{H}_{31}\text{O}_2\text{Si}_2$ 343.1761(M^+-^tBu), Found
343.1754

30 Step 6

Isopropenylmagnesium bromide (2 ml, 0.6M-THF sol.,
1.2 mmol) was added to 2 ml of a THF solution of diepox-
ide (82 mg, 0.21 mmol) and CuI (5 mg, 0.03 mmol) at -20
 $^\circ\text{C}$, and the mixture was stirred at $-15\text{ }^\circ\text{C}$ for 4 hours. A
35 saturated solution of ammonium chloride was added to the

reaction solution, and the solution was extracted with ether. The ether layer was washed with water, with saturated sodium bicarbonate solution and with saturated sodium chloride solution. The ether layer was dried over
5 magnesium sulfate. The solvent was distilled away under reduced pressure and a crude product (111 mg) was obtained. The product was dissolved in 3 ml of dichloromethane, pyridinium chlorochromate (90 mg, 0.41 mmol) was added, and the mixture was stirred for 10 hours
10 at room temperature. 3g of silica gel was added to the reaction solution, and the solution was filtered with cerite. The solvent was distilled away from the filtrate and the residue was chromatographed over silica gel to obtain a ketone (60 mg, 89%).

15

m.p. 78-79 °C

$[\alpha]_D^{29} +18.3^\circ$ (c 0.71, CHCl_3)

IR (nujol) 1706 cm^{-1}

$^1\text{H-NMR}$ (300 MHz), CDCl_3 ; 0.04 (s, 3H), 0.11(s, 3H), 0.12
20 (s, 3H), 0.14(s, 3H), 0.89(s, 9H), 0.94(s, 9H), 1.45-
1.56(m, 2H), 1.74(s, 3H), 2.98(t. d, $J=9.5$, 5.4 Hz, 1H),
3.04-3.08(m, 2H), 3.09(d, $J=15.0$ Hz, 1H), 3.17(d, $J=15.0$
Hz, 1H), 4.12(d, $J=9.5$ Hz, 1H), 4.21-4.25(m, 1H), 4.81(s,
1H), 4.94(s, 1H),

25 MS m/e 425(M^+-CH_3), 73(100%)

HRMS calcd for $\text{C}_{22}\text{H}_{41}\text{O}_4\text{Si}_2$ 425.2543(M^+-CH_3),

Found 425.2549

Anal. calcd for $\text{C}_{22}\text{H}_{41}\text{O}_4\text{Si}_2$: C 62.68; H 10.06;

Found C 62.82; H 10.06.

30 Step 7

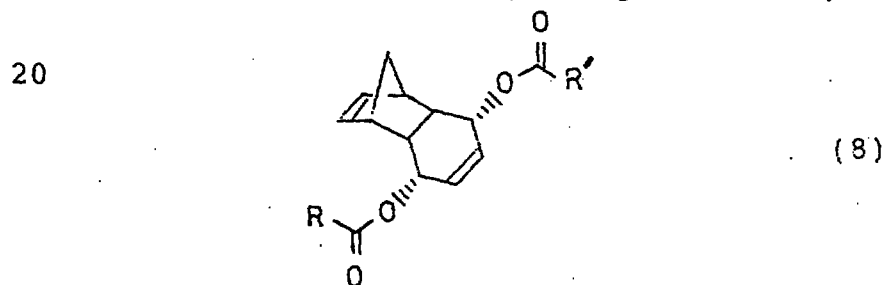
Bu_4NF (0.20 ml, 1M-THF sol. 0.2 mmol) was added to the enone (20 mg, 0.045 mmol) obtained by Step 6, and the mixture was stirred for one hour. After saturated sodium chloride solution was added, the mixture was extracted
35 with ethyl acetate, and the organic layer was dried over

magnesium sulfate. The solvent was distilled away under reduced pressure, and the residue was chromatographed over silica gel to obtain eutypoxide B (6.1 mg, 63%).

- 5 $[\alpha]_D^{23} -56.6^\circ$ (c 0.68, CHCl_3)
IR (film) 3414, 1678, 1614 cm^{-1}
 $^1\text{H-NMR}$ (300 MHz), CDCl_3 ; 1.50(t. d, $J=13.9$, 2.9 Hz, 1H),
1.80(t. d, 12.1 Hz, 2.8 Hz, 1H), 1.92(d, $J=1.1$ Hz, 3H),
2.06(d, $J=5.5$ Hz, 1H), 2.16(d, $J=0.7$ Hz, 3H), 2.67(ddd,
10 12.8, 9.5, 2.5 Hz, 1H), 2.89(d, $J=4.4$ Hz, 1H), 3.22(br. s, 1H), 3.25(d, $J=3.3$ Hz, 1H), 4.25(dd, $J=4.4$, 9.5 Hz, 1H), 4.36-4.42(m, 1H), 6.14(br. s, 1H)
MS m/e 212(M^+), 83(100%)
HRMS calcd for $\text{C}_{11}\text{H}_{16}\text{O}_4$ 212.1049(M^+), Found 212.1000

15 Example 8

To 30 ml of a phosphoric acid buffer containing 10% (v/v) acetone, 3,6-diacetyloxytricyclo [6,2,1,0^{2,7}] undeca-4,9-diene (8) (1.31 g, 5.0 mmol) was mixed.



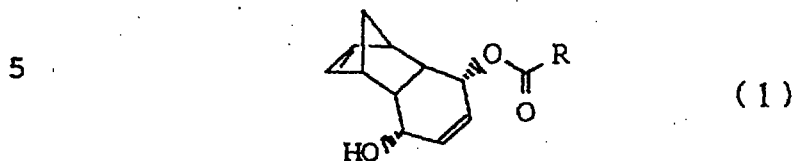
- 25 After lipase PS (30 mg) was added, and the mixture was shaken at 27°C. After 24 hours, the reaction solution was filtered with cerite, the filtrate was extracted with ether. The organic layer was dried over magnesium sulfate, and the solvent was distilled away under
30 reduced pressure. The residue was purified with a chromatograph over silica gel to obtain a monoacetate (1') (930 mg, 4.23 mmol, 85%). The specific rotation of the monoacetate was $[\alpha]_D^{29} -62.8^\circ$ (c2.0, CHCl_3). Further, the data of $^1\text{H-NMR}$ fit in with those of the
35 compound (1) of Example 1.



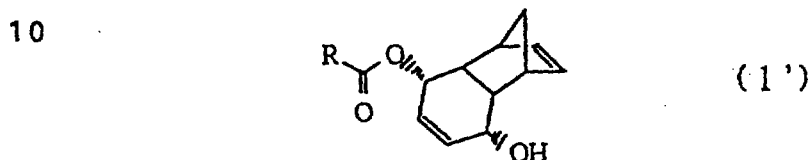
CYCLOHEXENE AND CYCLOHEXENONE DERIVATIVES AND PROCESS FOR
PRODUCTION OF CYCLOHEXENE DERIVATIVES

Claims

1. An optically active cyclohexene derivative represented by the general formula:

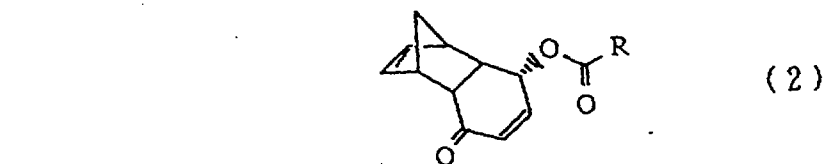


or

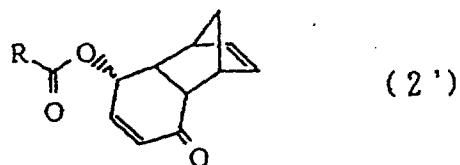


wherein R is alkyl.

2. An optically active cyclohexenone derivative
15 represented by the general formula:

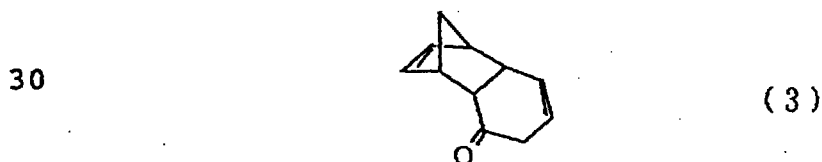


20 or



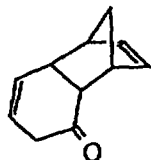
25 wherein R is alkyl.

3. An optically active cyclohexenone derivative
represented by the following formula:



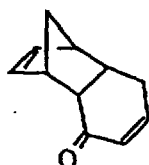
or

35



(3')

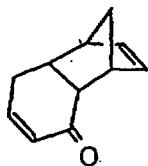
- 5 4. An optically active cyclohexenone derivative
represented by the formula:



(4)

10

or

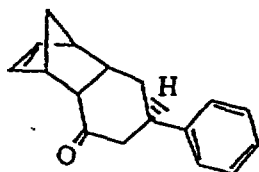


(4')

15

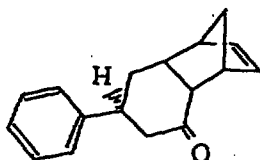
5. An optically active cyclohexanone derivative
represented by the following formula:

20



(5)

25 or



(5')

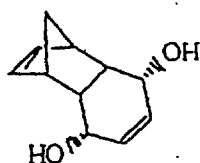
30

6. A process for producing an optically active cyclo-
hexene derivative comprising using the cyclohexene diol
represented by the following formula as a starting material:

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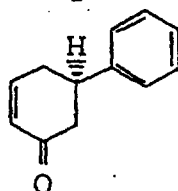
(6)

and subjecting the cyclohexene diol to transesterification at a position selectively to obtain the optically active cyclohexene derivative represented by the formula (1) or (1') of Claim 1.

7. A process according to claim 6, in which the cyclohexene diol is transesterified in the presence of lipase to obtain the optically active derivative.

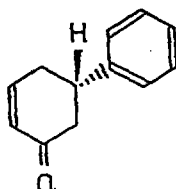
8. A process according to claim 6, in which the cyclohexene diol is unselectively transesterified and the diester subsequently selectively hydrolyzed in the presence of lipase.

9. A process for producing an optically active cyclohexenone derivative comprising using an optically active cyclohexenone derivative represented by the formula (2) or (2') of claim 2 as a starting material and, by way of an optically active cyclohexenone derivative represented by the formula (3) or (3'), an optically active cyclohexenone derivative represented by the formula (4) or (4') and an optically active cyclohexanone derivative represented by the formula (5) or (5'), obtaining the optically active cyclohexenone derivative represented by the following formula:



(7)

or



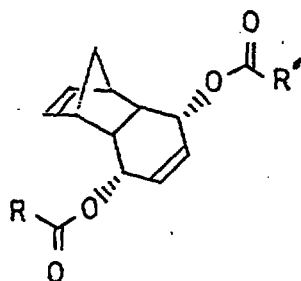
(7')

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10. A process for producing an optically active cyclohexene derivative comprising using a diacyloxy cyclohexene derivative represented by the following formula as a starting material, wherein R and R' are the same or different and each represents an alkyl group:



(8)

and reacting the diacycloxy cyclohexene derivative in the presence of lipase by stereoselective hydrolysis to obtain the optically active cyclohexene derivative represented by the formula (1) or (1') of claim 1.

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