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A novel synthetic method for (*R*)- and (*S*)-muscones by enantioselective hydrogenation of (*E*)- and (*Z*)-3-methyl-2-cyclopentadecen-1-ones catalyzed by *p-tolyl*-BINAP-Ru(II) complexes

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Abstract—A novel and practical synthesis of (*R*)- and (*S*)-muscones by the asymmetric hydrogenation of (*E*)- and (*Z*)-3-methyl-2-cyclopentadecen-1-ones catalyzed by *p-tolyl*-BINAP-Ru(II) complexes has been achieved in nearly complete enantioselectivity. © 2002 Published by Elsevier Science Ltd.

1. Introduction

Catalytic asymmetric synthesis has made remarkable advances in the last decade. Particularly, the recent progress achieved in the enantioselective hydrogenation of unsaturated compounds, has been remarkable and a number of important natural products have been synthesized in optically pure forms based on enantioselective hydrogenation. In these successful hydrogenations, the presence of certain kinds of chelating groups in a molecule is essential, and most of the successful enantioselective hydrogenations have been achieved using polyfunctionalized compounds.[1] From this viewpoint, further intensive hydrogenation is required to extend the successful enantioselective hydrogenation to important natural products which have a rather simple functionality. One of the unsolved target molecules for the catalytic asymmetric synthesis is muscone (**3**), which is a 15-membered simple cyclic ketone. Muscone (**3**) is one of the most important fragrance compounds, but it is isolated only in small quantities from the scent gland of the male musk-deer in Tibet, China and Laos, which are on the endangered species list. Therefore, an efficient asymmetric synthesis of **3** is highly desired. After Ruzicha[2] determined the structure of **3** as (*R*)-3-methylcyclopentadecanone in 1926, intensive investigations have been carried out on its total synthesis, and there appeared several good synthetic methods for racemic **3**.[3] However, the synthesis of **3** in an optically active form remained a difficult problem. The asymmetric synthesis of **3** so far reported[4] was a multistep synthesis starting from chiral building blocks such as (*R*)-citronellal,[4a,c,h,i] (*S*)-hydroxyisobutyric acid,[4b] (*R*)-6-oxo-3-methylhexanoate,[4d] (*R*)-3-methyl-*N*-phenylglutamic acid,[4e] (*S*)-4-bromo-3-methylbutanenitrile,[4f] and (*S*)-3-bromo-2-methylpropanol.[4g] Recently, as a short route to (*R*)-muscone, the enantioselective Michael addition of a chiral alkoxydimethylcuprate,[5a–g] di-*t*-butyl malonate[5f] and dimethylzinc-alkoxycupurate[5g] to (*E*)-2-cyclopentadecenone (**7**) has been achieved. As other short routes to the highly enantioselective (*R*)-**3**, the methods using homochiral ketals of the enone **7** and 3-methyl-2-cyclopentadecen-1-one (**2**) have also been reported. One is the diastereomeric Simmons–Smith cyclopropanation[6a] of the homochiral ketal of the enone **7** and the other is the asymmetric hydrogenation[6b,c] of the homochiral ketal of the enone **2** with the Ru-BINAP catalyst. However, these methods appear troublesome from a practical point of view. A practical synthetic route seemed to be the asymmetric hydrogenation of the enone **2**. Needless to say, the success of this method entirely depends on whether a high enantioselectivity during the hydrogenation can be achieved. Only few examples of the successful asymmetric hydrogenation of enones are known. For example, the hydrogenation of 2-alkylidenecyclopentanone with BINAP-Ru(II) complexes as the catalyst in 94–98%ee[7] and the hydrogenation of 3-methyl-2-cyclopenten-1-one with BPPM–Rh complexes as the catalyst in 30%ee.[8]

We now wish to present a solution to this problem. Namely, we wish to report the novel total synthesis of natural (*R*)-muscone as well as the unnatural (*S*)-muscone in high optical purity in a short number of steps by the highly enantioselective hydrogenation of the 15-membered cyclic

Keywords: asymmetric hydrogenation; *p-tolyl*-BINAP-Ru(II); (*E*)- and (*Z*)-3-methyl-2-cyclopentadecen-1-one; (*R*)- and (*S*)-muscone.

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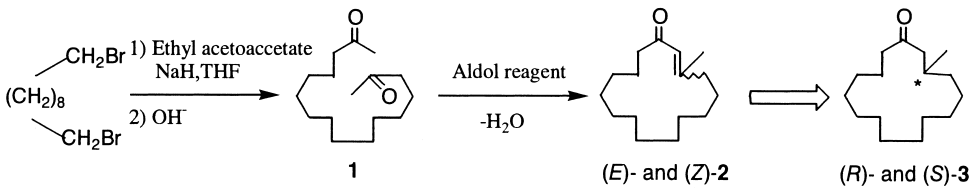


Scheme 1. Synthetic route to (*R*)- and (*S*)-**3**.

(*E*)- and (*Z*)-enones catalyzed using the *p-tolyl*-BINAP-Ru complexes as the key step.[9]

2. Results and discussion

The short synthetic route to chiral **3** in the present work is shown in Scheme 1. The key intermediate **2** had been prepared by the intramolecular aldol condensation reaction of 1,15-hexadecandione (**1**) via the Mg,[10] Al,[3a,b,11] Ti[12] and Zn[13a] enolates. Although the substrate **1** had been prepared by several ways such as from 1,10-dibromodecane[13] or 1,9-decadiene,[14] we prepared the dione **1** by the reaction with ethyl acetoacetate and 1,10-dibromodecane using sodium hydride as the base, and subsequently the cyclic enone **2** by the organoaluminum compound-mediated aldol condensation of the dione **1** according to the Tsuji method.[3a,b] The enone **2** prepared by this method was a mixture of (*E*)- and (*Z*)-isomers, the ratio of which depended on the reaction conditions.

They can be separated from each other by chromatography, and we separately investigated the asymmetric hydrogenation of the both the (*E*)- and (*Z*)-isomers.

Representative results of the asymmetric hydrogenation of the (*E*)-**2** and the (*Z*)-**2** are shown in Table 1.

Hydrogenation of the (*E*)-**2** or the (*Z*)-**2** was successfully carried out under mild conditions (25°C, 70 atm). The catalytic species of the *p-tolyl*-BINAP-Ru(II) complexes[15–17] had a significant influence on the catalytic activities as well as the enantioselectivity. Among the complexes used as the catalyst, the complex bearing a chloride ion, Ru_2Cl_4 [(*S*)-*p-tolyl*-binap]$_2$NEt$_3$ {(*S*)-**4**}, showed the highest catalytic activity and enantioselectivity (>98%ee at *S*/*C*=100) compared to those of the acetate complex (*S*)-**5** and the iodide complex (*S*)-**6** (runs 1, 3 and 4).

Table 1. Asymmetric hydrogenation of the enone (*E*)- and (*Z*)-**2** catalyzed by *p-tolyl*-BINAP-Ru(II) complexes

Run	Substrate	Cat.[a]	Reaction time (h)	Conv.[b]	Select.[b]	Product	%ee[c]
1	(*E*)-**2**	(*S*)-**4**	24	100	>98	(*R*)-**3**	>98[d]
2	(*E*)-**2**	(*R*)-**4**	24	100	>98	(*S*)-**3**	>98[d]
3	(*E*)-**2**	(*S*)-**5**	48	63	>98	(*R*)-**3**	84
4	(*E*)-**2**	(*S*)-**6**	48	92	96	(*R*)-**3**	18
5	(*Z*)-**2**	(*S*)-**4**	24	100	>98	(*S*)-**3**	>98
6	(*Z*)-**2**	(*R*)-**4**	24	100	>98	(*R*)-**3**	>98

Reactions conditions: substrate, 1 mmol; catalyst, 10^{-2} mmol; solvent, MeOH 10 ml; temperature, 25°C; pressure, 70 atm.

[a] **4**: Ru_2Cl_4(*p-tolyl*-binap)$_2$Net$_3$;[15] **5**: Ru(OCOCH$_3$)$_2$(*p-tolyl*-binap);[16] **6**: [RuI(*p-tolyl*-binap)(*p*-cymene)]I.[17]

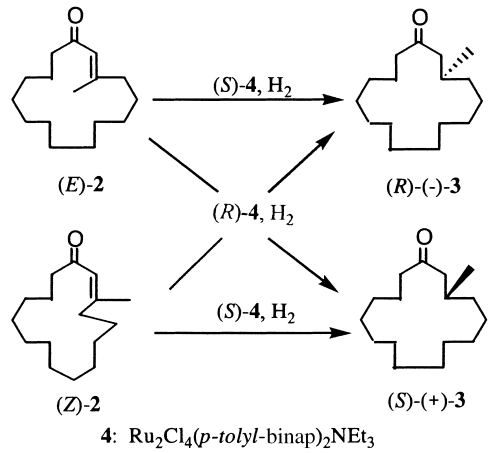
[b] Conversion and selectivity were determined by gas chromatography.

[c] Enantiomeric excess was determined by 400 MHz NMR using Eu (HFC)$_3$ as the chiral shift reagent.[4b]

[d] Optical rotation values, (*R*)-**3** (run 1): $[\alpha]_D^{25}=-12.3°$ (*c* 1.20, MeOH), (*S*)-**3** (run 2): $[\alpha]_D^{25}=+12.4°$ (*c* 1.10, MeOH).

The enantiomeric excess of **3** was determined to be higher than 98%ee by NMR spectroscopy using Eu(HFC)$_3$ as the chiral shift reagent[4b] (runs 1, 2, 5 and 6).

As shown in the asymmetric hydrogenation of geraniol and nerol[18] with the Ru-BINAP catalyst, it had been observed that the stereochemistry of the product depends on the configuration of the Ru-BINAP catalyst and the substrate. Similarly, in the present asymmetric hydrogenation, it has been observed that the stereochemistry of **3** depends upon the configuration of the catalyst **4** and the substrate **2**. That is (*R*)-muscone {(*R*)-**3**} was obtained from (*E*)-**2** by using complex (*S*)-**4**, and also from (*Z*)-**2** by using complex (*R*)-**4**. On the contrary, (*S*)-**3** was obtained from (*E*)-**2** by using complex (*R*)-**4** and also from (*Z*)-**2** by using complex (*S*)-**4** as shown in Scheme 2 (runs 1, 2, 5 and 6).



Scheme 2. The stereochemical dependency of **3** up on the configuration of catalyst **4** and the substrate **2**.

Thus, the present asymmetric hydrogenation has opened a new practical route to the optically pure (*R*)-**3**.

3. Experimental

3.1. General

Column chromatography was performed on silica gel (70–230 mesh). GC analyses were performed using a Hewlet-Packard model 5890 instrument equipped with a capillary column (Carbowax 20 M phase 0.2 mm ID×25 m, OV-1 0.2 mm ID×25 m). IR spectra were recorded on a JASCO

IR-810 spectrophotometer. The 400 MHz ^{1}H NMR spectra were recorded on a Bruker-AMX400 in $CDCl_3$ or C_6D_6 with TMS as the internal standard. The optical purity of muscone was determined by the 400 MHz ^{1}H NMR using $Eu(HFC)_3$ {*tris*-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate]-europium (III)} as the chiral shift reagent. Mass spectra (MS) were obtained using a Hitachi M-80B mass spectrometer. Optical rotations were recorded with a JASCO DIP-360 spectropolarimeter.

3.1.1. Synthesis of 2,15-hexadecanedione (1). Ethyl acetoacetate (130 g, 1.0 mol) was added dropwise to a solution of sodium hydride (60% dispersion in mineral oil, 40 g, 1.0 mol) in THF (300 ml) with stirring. Then 1,10-dibromodecane (75 g, 0.25 mol) was added dropwise to the mixture at refluxing temperature with stirring for 1.5 h and the reaction solution was refluxed and stirred for 14 h.

The mixture was filtered to remove the solid NaBr at room temperature (rt) and the filtrate was washed with 10% HCl solution. After removal of the solvent (THF), a 10% aqueous solution of NaOH (1.0 mol) was added to the mixture at rt and the mixture was stirred for a further 8 h to hydrolyze the di-keto-ester. The reaction mixture was washed with hexane (150 ml) and separated to extract any unreacted raw materials and by-products into the hexane layer. The water layer containing the sodium salt of the di-ketocarboxylic acid was acidified using 50% aqueous solution of H_2SO_4 (1.0 mol) at rt. The mixture was then stirred for 3 h at refluxing temperature for the decarboxylation. After adding THF (150 ml) to the reaction mixture, the mixture was washed and separated. The THF layer was then cooled to crystallize the crude solid of the dione **1**. The crude **1** was recrystallized from methanol to give colorless crystals **1** (28.5 g, 44%); mp 82–83°C (lit.[19]; mp 83–84°C); IR (neat) (cm^{-1}) 2920, 2840, 1710. ^{1}H NMR ($CDCl_3$); δ 1.26 (m, 16H), 1.56 (m, 4H), 2.13 (s, 6H), 2.41 (t, 4H, J=7.4 Hz). MS *m*/*z* (%): 254 (6, M^+), 197 (24), 179 (15), 138 (9), 123 (15), 109 (22), 95 (33), 83 (37), 71 (74), 58 (100), 43 (96).

3.1.2. Synthesis of 3-methyl-2-cyclopentadecen-1-one {(*E*)-2 and (*Z*)-2}. A solution of phenol (8.2 g, 88 mmol) in THF (400 ml) was placed in a three-necked flask with a reflux condenser and cooled to 0°C. A hexane solution of *i*-Bu_2AlH (80 ml; 80 mmol) was added dropwise to the flask at 0°C with stirring. Pyridine (7.6 g, 96 mmol) and hexane (1.6 l) were then added at rt. A solution of the dione **1** (5 g, 20 mmol) in THF (400 ml) and hexane (400 ml) was added dropwise over 15 h at refluxing temperature with vigorous stirring. The reaction mixture was stirred for an additional 3 h. The mixture was cooled to 0°C, and 3N-HCl was added. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with 5% NaOH solution, brine, and dried over $MgSO_4$. The product obtained by concentration of the extract was purified by column chromatography (silica gel, hexane/EtOAc 20:1) to give the crude enone **2** as a mixture of the geometric isomers (2.4 g, 51%) which consist of (*E*)-**2** (50%), (*Z*)-**2** (40%), and (*E*)- and (*Z*)-3-methyl-3-cyclopentadecen-1-one (10%). The crude enone **2** was repurified by column chromatography (silica gel, benzene) to give the pure (*E*)-**2**: IR (neat) (cm^{-1}): 2920, 2850, 1690, 1620, 1460, 1390, 1220, 1060, 980, 890. ^{1}H NMR (C_6D_6); δ 1.20 (m, 18H), 1.50 (m, 2H), 1.88 (m, 2H), 2.17 (s, 3H), 2.24 (t, 2H, J=6.6 Hz), 5.91 (s, 1H). MS *m*/*z* (%): 236 (17, M^+), 221 (10), 193 (4), 179 (4), 137 (4), 110 (35), 95 (100), 83 (77), 55 (52), 41 (77).

Pure (*Z*)-**2** was also separated from the crude enone **2** by other column chromatography conditions (silica gel impregnated with $AgNO_3$, hexane/EtOAc 100:1).

The (*Z*)-**2**: IR (neat) (cm^{-1}): 2920, 2850, 1690, 1620, 1460, 1380, 1120, 1080, 860, 810. ^{1}H NMR (C_6D_6): δ 1.31 (m, 18H), 1.54 (s, 3H), 1.60 (m, 2H), 2.19 (m, 2H), 2.82 (t, 2H, J=6.7 Hz), 5.83 (s, 1H). MS *m*/*z* (%): 236 (24, M^+), 221 (10), 193 (4), 137 (6), 110 (51), 95 (82), 55 (78), 41 (100).

3.1.3. General method for preparation of (*R*)- and (*S*)-muscone {(*R*)-3 and (*S*)-3}. The degassed mixture of the (*E*)-**2** (236 mg, 1 mmol) and Ru_2Cl_4 [(*S*)-*p*-*tolyl*-binap]$_2$-NEt_3 (9 mg, 10^{-2} mmol) in MeOH (10 ml) was stirred under hydrogen pressure (70 atm) in an autoclave at 25°C for 24 h. After evaporation of the solvent, the crude product was purified by silica gel column chromatography (hexane/EtOAc 20:1) to give (*R*)-**3**: $[\alpha]_D^{25}=-12.3°$ (*c* 1.1, MeOH).

IR (neat) (cm^{-1}) 2928, 2857, 1711. ^{1}H NMR (C_6D_6); δ 0.94 (d, 3H, J=6.7 Hz), 1.28 (m, 20H), 1.64 (m, 2H), 2.05 (m, 1H), 2.18 (dd, 1H, J=5.2, 15.0 Hz), 2.41 (t, 2H, J=6.9 Hz), 2.42 (dd, 1H, J=8.3, 15.0 Hz). MS *m*/*z* (%): 238 (40, M^+), 223 (11), 209 (18), 180 (16), 125 (40), 97 (42), 85 (100), 69 (44), 55 (44). (*S*)-**3** is also synthesized in the same manner as for (*R*)-**3** using Ru_2Cl_4 [(*R*)-*p*-*tolyl*-binap]$_2NEt_3$ instead of Ru_2Cl_4 [(*S*)-*p*-*tolyl*-binap]$_2NEt_3$ as the catalyst.

The enantioexcess of the (*R*)-**3** was determined to be more than 98%ee by the following NMR method. To the solution of $CDCl_3$ (0.70 ml) and $Eu(HFC)_3$ (150 mg), the (*R*)-or (*S*)-**3** (5 mg) was added, and the solution was subjected to analysis by NMR at 305 K. The peak (doublet) caused by the methyl group of the (*R*)-**3** shifted to 3.93 ppm, while that of the (*S*)-**3** shifted to 3.82 ppm. Both peaks were perfectly separated and a base line was down. We judged the value of the enantioexcess of the (*R*)-**3** to be more than 98%ee because the spectrum of the (*R*)-**3** did not show any peak at 3.82 ppm caused by the methyl group of the (*S*)-**3**, but that of the mixture of the (*R*)-**3** (99%) and the (*S*)-**3** (1%) showed a very small peak at 3.82 ppm. The ee value of (*S*)-**3** was also determined to be more than 98%ee in a similar manner.

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