February, 1991] © 1991 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 64, 387—391 (1991) 387

Asymmetric Diels-Alder Reactions of an Acrylic Acid Derivative Using a Chiral Titanium Catalyst

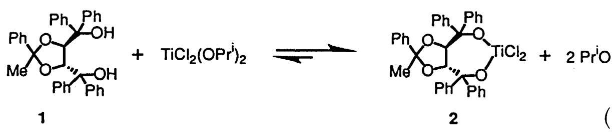
Koichi Narasaka,* Hiroko Tanaka, and Fumihiko Kanai
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

(Received September 26, 1990)

Asymmetric Diels-Alder reactions of an acrylic acid derivative using a catalytic amount of a chiral titanium reagent were performed with several dienes. The titanium catalyst was prepared by the alkoxy exchange between dichlorodiisopropoxytitanium(IV) and a chiral 1,4-diol derived from (2*R*,3*R*)-tartrate. By the use of the titanium catalyst, the reaction between 3-acryloyl-1,3-oxazolidin-2-one and dienes proceeded in a toluene-petroleum ether mixture in the presence of Molecular Sieves 4A to afford the Diels-Alder adducts in 72—100% yields and 88—>96% enantioselectivity. This reaction can be applied to a diene containing a hetero atom such as 2-ethylthio-1,3-butadiene, which affords the Diels-Alder adduct in a high optical purity. In this paper are also described the methods for determining the optical purities of the obtained 4-substituted 3-cyclohexenecarboxylic acid derivatives.

Diels-Alder reaction is one of the most important reaction for the formation of carbon frameworks in a variety of organic compounds, and has been widely used as a key step in the synthesis of many kinds of natural products. Development of asymmetric Diels-Alder reaction has been in active research,[1] however, the catalytic reaction with a wide applicability and a high enantioselectivity is scarce.

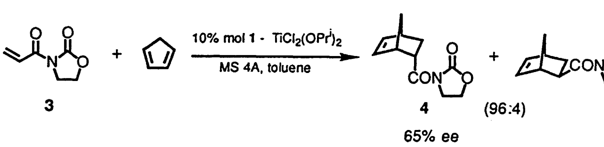
In our laboratory, the exploration of asymmetric reactions, including asymmetric Diels-Alder reaction, has been investigated using a chiral titanium catalyst prepared by an alkoxy exchange between a tartrate derived 1,4-diol (**1**) and dichlorodiisopropoxytitanium(IV) (Eq. 1).[2]



(1)

We have already found that when 3-(2-alkenoyl)-1,3-oxazolidinone derivatives were used as dienophiles, the reaction with several dienes proceeded in a toluene-petroleum ether (P.E.) mixture in the presence of a catalytic amount of the titanium catalyst and Molecular Sieves (MS) 4A to yield the Diels-Alder adducts in more than 90% enantiomeric excess (ee).[3]

The Diels-Alder adducts of acrylic acid derivatives constitute an important class of compounds as key intermediates for the total synthesis of a variety of natural products.[4] The catalytic asymmetric Diels-Alder reaction was also performed with 3-acryloyl-1,3-oxazolidin-2-one (**3**). However, the only result obtained so far was the reaction carried out in toluene, which afforded the Diels-Alder adduct **4** with cyclopentadiene in only 65% ee[5] and the reaction had never been carried out in the mixed solvent (toluene-petroleum ether (P.E.)) which has been found to be the most suitable solvent in the reaction of other α,β-unsaturated carboxylic acid derivatives.[3] Therefore some modifications in the reaction conditions have to be made to obtain synthetically useful 4-substituted 3-cyclohexenecarboxylic acid derivatives in high optical purities.

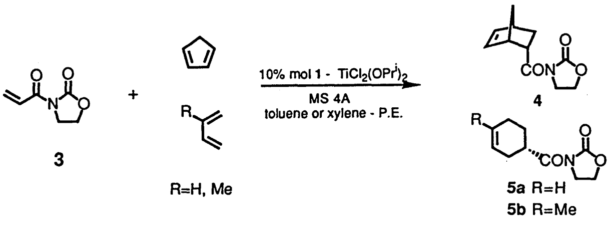


(2)

At the same time there arose a need for the development of a method for determining the accurate optical purities of the obtained Diels-Alder adducts, the 4-substituted 3-cyclohexenecarboxylic acid derivatives, since the method for the determination of the optical purities of these products was limited to transforming them to some compounds whose optical rotations are known.[6,7] Such a method lacks in accuracy especially when the enantioselectivities are very high.

In this paper, the reaction conditions using an acrylic acid derivative **3** were optimized to give the Diels-Alder adducts in good to high enantioselectivity, and the method for determining accurate optical purities of the adducts has been developed.

First, the reactions of **3** and several dienes were performed in a mixed solvent of toluene or xylene and P.E. in the presence of MS 4A. (Eq. 3) The results are



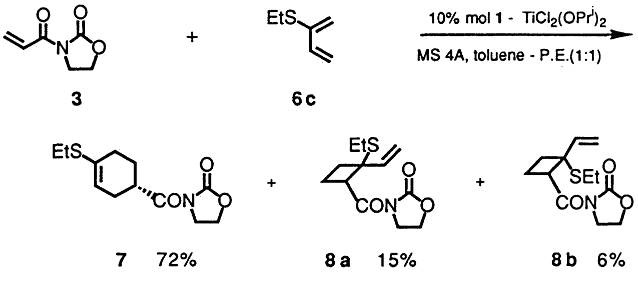
(3)

Table 1. Diels-Alder Reaction Using a Catalytic Amount of **1**

Diene	Solvent	Temp, θ/ °C	Time	Yield/%	Opt. purity/%ee
Cyclopentadiene	Toluene-P.E.(1 : 1)	−23	24 h	81(12)[a]	88
	p-Xylene-P.E.(1 : 1)	0	3 h	96	75
	m-Xylene-P.E.(1 : 1)	0	12 h	Quant	82
Isoprene	Toluene-P.E.(1 : 1)	0	24 h	89	>96
	p-Xylene-P.E.(1 : 1)	0	12 h	93	>96
	m-Xylene-P.E.(1 : 1)	0	12 h	90	>96
Butadiene	Toluene-P.E.(1 : 1)[b]	RT	6 d	31(46)	88
	p-Xylene-P.E.(1 : 1)[c]	RT	24 h	81	93
	m-Xylene-P.E.(1 : 1)[c]	RT	2 d	67	89

a) Amount of the recovered **3** is shown in ( ). b) 10 mol% catalyst was used. c) 20 mol% catalyst was used.

listed in Table 1.

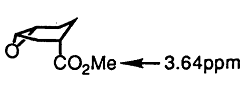


(4)

By the use of a mixed solvent, toluene-P.E. (1 : 1), the reaction of **3** with cyclopentadiene proceeded at −23 °C in the presence of 10% mol of the chiral titanium reagent and MS 4A to give the cycloadduct **4**. Only the endo isomer **4** was obtained and the optical purity of the obtained adduct was found to be greatly enhanced from 65 to 88% ee. In the reaction with 1,3-butadiene, the best result was observed when the reaction was carried out at room temperature in a *p*-xylene-P.E. (1 : 1) mixed solvent using 20% mol of the chiral catalyst, and the optical purity of the adduct **5a** was 93% ee. The reaction with isoprene proceeded at 0 °C using 10% mol of the chiral catalyst and the optical purity of the adduct **5b** was over 96% ee in either toluene-P.E. or xylene-P.E. mixed solvent. In this case too, the obtained cycloadduct consisted of a single isomer and none of the other regio-isomer could be detected. After all, the use of toluene or xylene in the mixed solvent made little or no influence on the optical purity of the obtained product. When 2 molar amounts of the chiral titanium catalyst were used, the reaction proceeded at lower temperatures, but that does not alter the enantioselectivity to a great extent. Next, to obtain a masked cyclohexanone derivative, which is an important synthetic intermediate, the reactions of dienes with a hetero atom were examined. 2-*t*-Butyldimethylsiloxy-1,3-butadiene (**6a**)[8] and 2-methoxy-1,3-butadiene (**6b**)[9] were employed as dienes, but the reaction did not proceed well. With **6a**, the titanium seemed to exchange with the silyl part of the diene and therefore the reaction did not proceed. With **6b**, decomposition of the diene took place prior to the Diels-Alder reaction. 2-Ethylthio-1,3-butadiene (**6c**)[10] containing a sulfur atom instead of an oxygen atom was then examined. With **6c**, the acryloyloxazolidinone **3** reacted smoothly at 0 °C within 2 h in a toluene-P.E. (1 : 1) mixed solvent to afford the adduct **7** in 72% yield and in 91% optical purity along with cyclobutanes **8a** and **8b** (Eq. 4). The *trans* **8a** and *cis* **8b** isomers of the cyclobutane were obtained in 15 and 6% yields, respectively, which are the [2+2] cycloaddition products as we have already reported in the cycloaddition reaction between α,β-unsaturated carbonyl compounds and a ketene dithioacetal, an alkenyl sulfide and an alkynyl sulfide.[11] The obtained Diels-Alder adduct **7** has a vinyl sulfide group, which is easily transformed to some other functional groups.

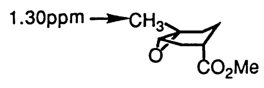
As mentioned in the beginning, the precise optical purity of the obtained Diels-Alder products, 4-substituted 3-cyclohexenecarboxylic acid derivatives, had never been determined. The optical purities of the cyclohexenecarboxylic acid derivatives **5a** and **5b** prepared above were determined after transformation to the epoxy derivative **12** based on the following Scheme 1.

First the adducts **5a** and **5b** were hydrolyzed to the corresponding carboxylic acids after they were transformed into their methyl esters. The iodolactonization of the carboxylic acids followed by the treatment with sodium methoxide gave the corresponding *cis*-epoxy carboxylic esters (**12a,b**). The optical purities were determined by adding a chiral shift reagent Eu(hfc)$_3$[12] and analyzing their NMR. The methoxyl



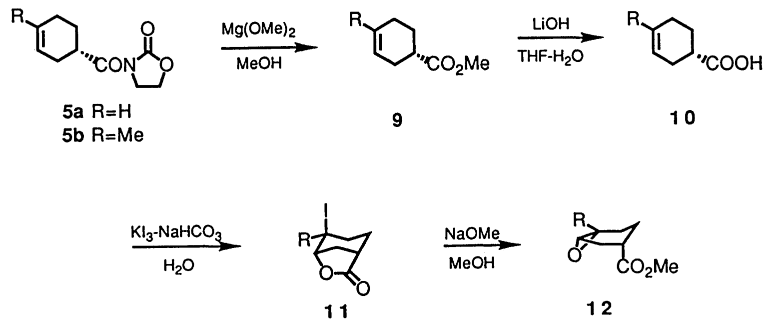
12a

Fig. 1.



12b

Fig. 2.

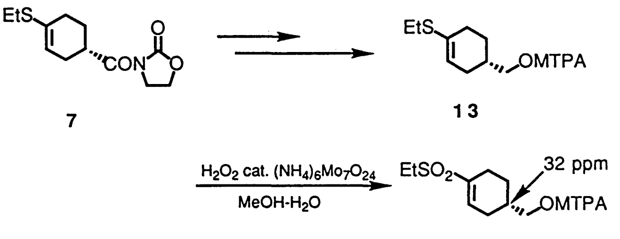


Scheme 1.

peak (δ=3.64) of **12a** (Fig. 1), and the methyl peak (δ=1.30) of **12b** (Fig. 2) were used to determine the optical purities.

The optical purity of the norbornene derivative **4**, was determined by the Mosher's method[13] after the adduct was esterified and reduced with $LiAlH_4$.

In the case of **7**, the product was first transformed into its (+)-trifluoromethylmethoxyphenylacetic acid (MTPA) ester and then the sulfide **13** was oxidized to the sulfone **14** by hydrogen peroxide and $(NH_4)_6Mo_7O_{24}$ catalyst (Eq. 5).[14] Its optical purity was determined by measuring the ^{13}C NMR spectrum. The peak of the chiral center of the cyclohexene ring (δ=32)[15] separated completely.



(5)

The absolute configuration of the norbornene derivative **4** was determined by the comparison of its optical rotation with those of the literatures.[3] For the cyclohexene derivatives **5a** and **5b** the obtained adducts were transformed to their benzyl (in the case of **5a**) or methyl (in the case of **5b**) esters and their optical rotations were measured and compared with those of the literatures.[6,7]

Combined with the results of the previous paper,[3] the absolute stereoselection of the Diels-Alder reaction is predictable without any exceptions according to the transition model as depicted in Fig. 3. The chiral titanium species is thought to form a six-membered chelate with 3-acyl-1,3-oxazolidin-2-one, which exists in a pseudo C_2 symmetrical twist chair conformation. The axial phenyl groups in the seven-membered ring orient to the reaction site and restrict the approach of a diene. Therefore, *re*-face of the α-carbon of the unsaturated acid moiety is attacked preferentially in

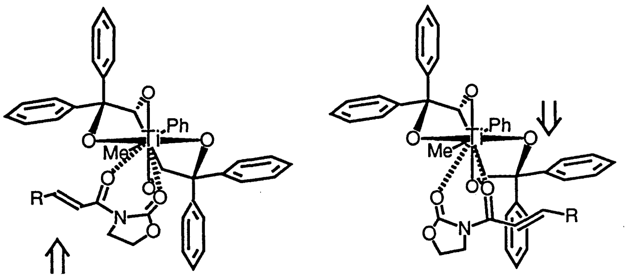


Fig. 3.

both of the possible transition states shown in Fig. 3, when the (2*R*,3*R*)-1,4-diol is employed as a chiral auxiliary.

In summary, the Diels-Alder reaction of acrylic acid derivative using a catalytic amount of the chiral titanium reagent proceeded to produce the adducts in good yields and in good enantioselectivities. The reaction was carried out in a toluene-P.E.(1 : 1) mixed solvent in the presence of MS 4A. This catalytic asymmetric Diels-Alder reaction totally offers a practical and a convenient method for the preparation of variously substituted 3-cyclohexenecarboxylic acids via 3-alkenoyl-1,3-oxazolidin-2-one in general.

Experimental

General. NMR spectra were recorded on a Hitachi R24B or Bruker AM 500 spectrometer using tetramethylsilane as the internal standard. IR spectra were recorded on a Horiba FT-300S. Optical rotation was measured with a Nippon Bunko DIP-370. Mass spectra were obtained with a JEOL JMS-D300 mass spectrometer.

Dichlorodiisopropoxytitanium was prepared from titanium(IV) chloride and titanium(IV) isopropoxide according to the literature method.[16] Toluene was distilled and dried over MS 4A. Xylenes were distilled from CaH_2 and stored over MS 4A. Tetrahydrofuran was freshly distilled from sodium diphenylketyl.

(2*R*,3*R*)-1,1,4,4-tetraphenyl-2,3-*O*-(1-phenylethylidene)-1,2,3,4-butanetetrol (**1**) and 3-acryloyl-1,3-oxazolidin-2-one (**3**) were prepared according to the literature procedures.[3,7]

Preparation of 2-Ethylthio-1,3-butadiene (6c). 2-Ethylthio-1,3-butadiene was synthesized according to the literature procedure.[10] The crude product was purified by column chromatography using pentane as an eluent (37% yield). ^{1}H NMR (CDCl$_3$) δ=1.31 (t, 3H, *J*=7.4 Hz), 2.77 (q, 2H, *J*=7.4 Hz), 5.02 (s, 1H), 5.17 (d, 1H, *J*=10.0 Hz), 5.33 (s, 1H), 5.54 (d, 1H, *J*=17.2 Hz), and 6.44 (dd, 1H, *J*=10.0, 17.2 Hz).

Asymmetric Diels–Alder Reaction. General Procedure for the Reaction Using a Catalytic Amount of the Titanium Reagent. The reaction of 3-acryloyl-1,3-oxazolidin-2-one (**3**) with isoprene is outlined. To a toluene (4 ml) solution of dichlorodiisopropoxytitanium (145 mg, 0.611 mmol) was added the chiral diol **1**, (325 mg, 0.615 mmol) at room temperature under an argon atmosphere and the mixture was stirred for 1 h. This toluene solution of the chiral titanium catalyst (1 ml, 0.153 mmol) was added to powdered MS 4A under an argon atmosphere, and the mixture was cooled to −78 °C. A toluene (4 ml) solution of 3-acryloyl-1,3-oxazolidin-2-one (**3**) (216 mg, 1.53 mmol) was added to the mixture. Then P.E. (5 ml) and isoprene (1.5 ml) were added. The mixture was stirred overnight at 0 °C, and then pH 7 buffer was added to the mixture. The organic materials were extracted with ethyl acetate and the combined extracts were dried over anhydrous Na$_2$SO$_4$. After the evaporation of the solvent, the crude product was purified by thin-layer chromatography (silica gel, AcOEt : hexane=1 : 1) to give the pure product **5b** in 89% yield.

By the same procedure described above, the cycloaddition products **4**, **5a**, and **5b** were obtained.

Spectral data and physical properties of the cycloadducts are as follows:

3-[(1*S*,2*S*,4*S*)-Bicyclo[2.2.1]hept-5-en-2-ylcarbonyl]-1,3-oxazolidin-2-one (4). ^{1}H NMR and IR spectra agreed with those of the literatures.[2] $[\alpha]_D^{25}$ −132.5° (*c* 0.898, CH$_2$Cl$_2$), 88% ee, lit, $[\alpha]_D$ −65° (*c* 1.5, CH$_2$Cl$_2$), 38% ee.[3]

3-[(1*R*)-3-Cyclohexen-1-ylcarbonyl]-1,3-oxazolidin-2-one (5a). IR (KBr) 1776, 1695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.14—2.74 (m, 6H), 3.45—4.61 (m, 5H), and 5.65 (s, 2H); $[\alpha]_D^{23}$ −20.2° (*c* 1.75, CH$_2$Cl$_2$), 89% ee. HRMS Found: *m/z* 195.0890. Calcd for C$_{10}$H$_{13}$NO$_3$: M, 195.0896.

3-[(1*R*)-4-Methyl-3-cyclohexen-1-ylcarbonyl]-1,3-oxazolidin-2-one (5b). IR (KBr) 1776, 1689 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.68 (s, 3H), 1.75—2.40 (m, 6H), 3.72—4.95 (m, 5H), and 5.36 (br, 1H); $[\alpha]_D^{23}$ −38.8° (*c* 2.55, CH$_2$Cl$_2$), 96% ee. Anal. Calcd for C$_{11}$H$_{15}$NO$_3$: C, 63.14; H, 7.23; N, 6.69%. Found: C, 63.15; H, 7.18; N, 6.71%.

3-[(1*R*)-4-Ethylthio-3-cyclohexen-1-ylcarbonyl]-1,3-oxazolidin-2-one (7). IR (KBr) 1776, 1695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.26 (t, 3H, *J*=7.5 Hz), 1.77 (ddd, 1H, *J*=24.0, 11.0, 5.7 Hz), 2.01—2.06 (m, 1H), 2.20—2.25 (m, 1H), 2.30—2.39 (m, 3H), 2.68 (dq, 1H, *J*=12.5, 7.2 Hz), 2.71 (dq, 1H, *J*=12.5, 7.2 Hz), 3.73 (dddd, 1H, *J*=2.7, 5.8, 9.0, 15.0 Hz), 4.03 (t, 2H, *J*=8.3 Hz), 4.42 (t, 2H, *J*=8.3 Hz), and 5.61—5.63 (br, 1H); $[\alpha]_D^{26}$ −44.3° (*c* 0.859, CH$_2$Cl$_2$), 91% ee. HRMS Found: *m/z* 255.0902. Calcd for C$_{12}$H$_{17}$NO$_3$S: M, 255.0930.

Transformation of 5a and 5b into Their Epoxy Derivatives 12a and 12b. Formation of the Methyl Ester 9b. A few drops of carbon tetrachloride was added to magnesium (80.1 mg, 3.30 mmol). Then dry methanol (6.6 ml) was added under an argon atmosphere at 0 °C to generate magnesium methoxide. When all the magnesium dissolved, an ether (5 ml) solution of the Diels–Alder adduct **5b** (263 mg, 1.26 mmol) was added. The reaction was immediately quenched with saturated ammonium chloride and the methyl ester was extracted with ether. The organic layers were washed with brine and dried over anhydrous sodium sulfate. After the evaporation of the solvent, the crude product **9b** was directly used for further transformations.

Hydrolysis of 9b to the Carboxylic Acid 10b. A THF-water (10 : 1) mixture was added to the methyl ester **9b** (93.1 mg, 0.603 mmol) at room temperature until the ester completely dissolved. Then 2.5 equiv of lithium hydroxide monohydrate (62.9 mg, 1.50 mmol) was added to this solution at room temperature and the mixture was stirred for 8 h. After the evaporation of the solvent, 1M sodium hydroxide solution was added and the water layer was washed with ether. The water layer was made acidic with concd hydrochloric acid, and extracted with ether. The combined organic layers were dried over anhydrous sodium sulfate. After the evaporation of the solvent, the crude carboxylic acid was directly used for further transformations.

Iodolactone 11b. The carboxylic acid **10b** (40.0 mg, 0.285 mmol) was dissolved in 0.5M sodium hydrogencarbonate solution (1.7 ml). To this, an aqueous solution (4 ml) of iodine (148.0 mg, 0.583 mmol) and potassium iodide (285.0 mg, 1.72 mmol) was added and the mixture was stirred overnight at room temperature in the dark. The reaction mixture was diluted with water. Then aqueous Na$_2$S$_2$O$_3$ was added and the organic compounds were extracted with CH$_2$Cl$_2$. The combined organic layers were washed with saturated sodium hydrogencarbonate solution and dried over anhydrous sodium sulfate. After the evaporation of the solvent, the crude product (**11b**) (76.1 mg) was directly used for obtaining the epoxy derivative **12b**.

Epoxy Derivative 12b. NaOMe (17.1 mg, 0.317 mmol) was dissolved in dry methanol (3 ml) at 0 °C under an argon atmosphere. To this, a THF (3 ml) solution of the iodolactone **11b** (69.6 mg, crude) was added and the mixture was stirred overnight. The reaction mixture was quenched with a pH 7 phosphate buffer after the evaporation of methanol. The epoxy compound was extracted with ether and the combined organic layers were washed with water and brine successively, and dried over anhydrous sodium sulfate. After the evaporation of the solvent, the epoxy derivative **12b** was purified by TLC (hexane : AcOEt=4 : 1). (23.0 mg, 52% yield). The epoxy compound was analyzed by NMR with the addition of a chiral shift reagent, (Eu(hfc)$_3$).[12]

Spectral data of the epoxy compounds are as follows.

Methyl 3,4-Epoxycyclohexane-1-carboxylate (12a). **5a** was transformed to its epoxy derivative **12a** in the same manner. ^{1}H NMR (CDCl$_3$) δ=1.52—1.62 (m, 2H), 1.70—1.77 (m, 2H), 2.10—2.12 (m, 2H), 2.15—2.22 (m, 2H), 3.08 (s, 1H), and 3.64 (s, 3H).

Methyl 4-Methyl-3,4-epoxycyclohexane-1-carboxylate (12b). ^{1}H NMR (CDCl$_3$) δ=1.30 (s, 3H), 1.54—1.71 (m, 4H), 2.02—2.25 (m, 3H), 2.96 (d, 1H), and 3.64 (s, 3H).

Preparation of the MTPA Ester 13. The Diels–Alder adduct **4** was transformed to its benzyl ester by the literature method.[7] To reduce the benzyl ester to the corresponding alcohol, the THF (3 ml) solution of the benzyl ester was added to the mixture containing THF (1 ml) and LiAlH$_4$ (13.8 mg, 0.364 mmol) at 0 °C under an argon atmosphere. After 1 h, the reaction was quenched with saturated aqueous sodium sulfate and the organic materials were extracted with ether by decantation, and dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent afforded the crude product, which was purified by thin layer chromatography (benzene : ether=2 : 1, ×2) to give the pure product

(84% yield). The obtained alcohol was transformed to its MTPA ester **13** by the Mosher's method.[13]

Oxidation of the MTPA Ester to 14.[14] Methanol was added to (1*S*)-4-ethylthio-3-cyclohexen-1-ylmethyl (+)-trifluoromethylmethoxyphenylacetate (**13**) (9.2 mg, 0.024 mmol) until all of **13** had dissolved at 0 °C. Then 30% hydrogen peroxide (1 ml) and $(NH_4)_6Mo_7O_{24}$ (10 mg) were added and the mixture was stirred for 3.5 h. The sulfone (**14**) was extracted with CH_2Cl_2 and the combined organic layers were washed with brine and dried over anhydrous sodium sulfate. After the evaporation of the solvent, the crude product (10.1 mg) was analyzed by ^{13}C NMR without further purification. ^{1}H NMR ($CDCl_3$) $\delta=1.25$ (t, 3H), 1.26—1.37 (m, 1H), 1.89—2.09 (m, 2H), 2.24—2.50 (m, 3H), 2.89 (dq, 1H), 2.91 (dq, 1H), 3.51 (s, 3H), 4.16 (dd, 1H), 4.30 (dd, 1H), 6.72—6.76 (br, 1H), 7.37—7.43 (m, 3H), and 7.47—7.50 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta=7$, 23, 25, 28, 30, 31, 32, 47, 56, 69, 122, 128, 129, 130, 139, and 167.

References

1) L. A. Paquette, "Asymmetric Synthesis," ed by J. D. Morrison, Academic Press, Inc., Orlando (1984), Vol. 3, p. 455; G. Helmchen, R. Karge, and J. Weetman, "Modern Synthetic Methods," ed by R. Scheffold, Springer-Verlag, Berlin (1986), Vol. 4, p. 262; W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, **23**, 876 (1984); D. A. Evans, K. T. Chapman, and J. Bisaha, *J. Am. Chem. Soc.*, **106**, 4261 (1984); S. Masamune, L. A. Reed, J. T. Davis, and W. Choy, *J. Org. Chem.*, **48**, 4441 (1983); T. R. Kelly, A. Whiting, and N. S. Chandrakumar, *J. Am. Chem. Soc.*, **108**, 3510 (1986); E. J. Corey, R. Imwinkelried, S. Pikul, and Y. B. Xiang, *ibid.*, **111**, 5493 (1989); K. Kishikawa, M. Yamamoto, S. Kohmoto, and K. Yamada, *J. Org. Chem.*, **54**, 2488 (1989); K. Maruoka, and H. Yamamoto, *J. Am. Chem. Soc.*, **111**, 789 (1989); K. Furuta, S. Shimizu, Y. Miwa, and H. Yamamoto, *J. Org. Chem.*, **54**, 1481 (1989).

2) N. Iwasawa, Y. Hayashi, H. Sakurai, and K. Narasaka, *Chem. Lett.*, **1989**, 1581.

3) K. Narasaka, N. Iwasawa, M. Inoue, T. Yamada, M. Nakashima, and J. Sugimori, *J. Am. Chem. Soc.*, **111**, 5340 (1989).

4) E. J. Corey, N. M. Weinshenker, T. K. Schaaf, and W. Huber, *J. Am. Chem. Soc.*, **91**, 5675 (1969); E. J. Corey and H. E. Ensley, *ibid.*, **97**, 6908 (1975); R. K. Boeckman, Jr., P. C. Naegely, and S. D. Arthur, *J. Org. Chem.*, **45**, 754 (1980); O. Ceder and H. G. Nilsson, *Acta Chem. Scand. B*, **30**, 908 (1976); E. E. Smissman, J. T. Suh, M. Oxman, and R. Daniels, *J. Am. Chem. Soc.*, **84**, 1040 (1962).

5) The optical purity was determined by converting the product into its benzyl ester and measuring its optical rotation.

6) H. M. Schwartz, W. Wu, P. W. Marr, and J. B. Jones, *J. Am. Chem. Soc.*, **100**, 5199 (1978).

7) D. A. Evans, K. T. Chapman, and J. Bisaha, *J. Am. Chem. Soc.*, **110**, 1238 (1988); J. Colonge and J. Crabalona, *Bull. Chim. Soc. Fr.*, **1960**, 102; H. B. Henbest and R. S. McElhinney, *J. Chem. Soc.*, **1959**, 1834.

8) E. Vedejs, T. H. Eberlein, D. J. Mazur, C. K. McClure, D. A. Perry, R. Ruggeri, E. Schwartz, J. S. Stults, D. L. Varie, R. G. Wilde, and S. Wittenberger, *J. Org. Chem.*, **51**, 1556 (1986).

9) L. J. Dolby and K. S. Marshall, *Org. Prep. Proced.*, **1** (**4**), 229 (1969); *Chem. Abstr.*, **72**, 344 (1970).

10) E. Negishi and F. T. Luo, *J. Org. Chem.*, **48**, 1562 (1983).

11) Y. Hayashi and K. Narasaka, *Chem. Lett.*, **1989**, 793; **1990**, 1295.

12) $Eu(hfc)_3$: tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III).

13) J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969).

14) M. Joaquina and S. A. Amaral, *J. Chem. Soc. C*, **1969**, 2495.

15) The peak assignment of the chiral center was done by measurement of DEPT. The chemical shifts of the two separated peaks were $\delta=31.76$ and 31.82. The intensities of the two signals were equal in the racemic compound of **14**.

16) C. Dijkgraaf and J. P. G. Rousseau, *Spectrochim. Acta, Part A*, **24**, 1213 (1968).