Remarkable Effect of Aluminum Reagents on Rearrangements of Epoxy Acylates via Stable Cation Intermediates and Its Application to the Synthesis of (*S*)-(+)-Sporochnol A

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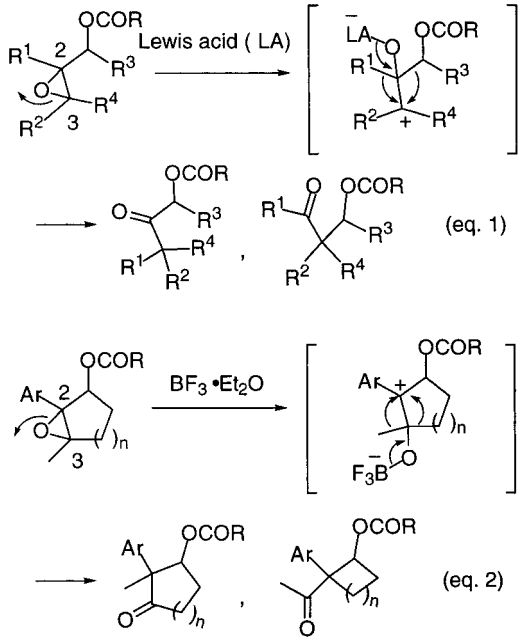
A remarkable effect of $(C_6F_5O)_3Al$ for promoting the rearrangement of epoxy acylates via stable cation intermediates was found, and new methods for constructing chiral benzylic, vinylic, and acetylenic quaternary carbon centers were developed. During the study, the importance of the ionic nature of the O−metal bond in the intermediates of such epoxides was addressed. This method was applied to the asymmetric total synthesis of (*S*)-(+)-sporochnol A.

Introduction

The rearrangement of epoxides is a useful tool to transform the carbon skeleton and has been extensively studied from both synthetic and theoretical points of view.[1] The ionic nature of O−A$^-$ bonds of intermediates obtained by acid (A−B) treatment of epoxides is an important factor to get fruitful results. In this paper, we report such examples in which the ionic nature of the O−A$^-$ bond plays an important role and its application.

After the development of many ways to obtain optically active epoxides exemplified by the Sharpless−Katsuki asymmetric epoxidation technology, it became easy to obtain optically active epoxides, and their rearrangements have provided good ways to obtain optically active carbonyl compounds.[2] In fact, many reports show that chiral aldehydes and ketones can be obtained by the rearrangement of optically active epoxides in high yields with high enantioselectivity.[3] We have also developed methods to obtain optically active carbonyl compounds having spiro skeletons or quaternary carbons by rearrangement of the 2,3-epoxy acylates, easily prepared in optically active forms.[4,5] We then attempted to construct chiral benzylic quaternary carbon centers by the rearrangement of the 3-aryl-2,3-epoxy acylates because many natural products have chiral benzylic quaternary carbon centers.[6]

Among our previous studies on the rearrangement of 2,3-epoxy acylates (eqs 1 and 2),[4,5] the following two



features are noteworthy: (i) the tetraalkyl substituted 2,3-epoxy acylates rearrange via the C3-cleavage of the oxirane rings (the C3-carbocation intermediates) as a

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(1) For reviews on the Lewis acid mediated rearrangement of epoxides, see: (a) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737−799. (b) Rickborn, B. In *Comprehensive Organic Synthesis, Carbon−Carbon σ-Bond Formation*; Pattenden, G., Ed.; Pergamon Press: Oxford, 1991; Vol. 3, Chapter 3.3, pp 733−775.

(2) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922−1925.

(3) Jung, M. E.; D'Amico, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 7379−7388 and references therein.

(4) (a) Fujioka, H.; Kitagaki, S.; Imai, R.; Kondo, M.; Okamoto, S.; Yoshida, Y.; Akai, S.; Kita, Y. *Tetrahedron Lett.* **1995**, *36*, 3219−3222. (b) Kita, Y.; Kitagaki, S.; Yoshida, Y.; Mihara, S.; Fang, D.-F.; Fujioka, H. *Tetrahedron Lett.* **1997**, *38*, 1061−1064. (c) Kita, Y.; Kitagaki, S.; Yoshida, Y.; Mihara, S.; Fang, D.-F.; Kondo, M., Okamoto, S.; Imai, R.; Akai, S.; Fujioka, H. *J. Org. Chem.* **1997**, *62*, 4991−4997. (d) Kita, Y.; Yoshida, Y.; Kitagaki, S.; Mihara, S.; Fang, D.-F.; Furukawa, A.; Higuchi, K.; Fujioka, H. *Tetrahedron* **1999**, *55*, 4979−4998.

(5) (a) Kita, K.; Kitagaki, S.; Imai, R.; Okamoto, S.; Mihara, S.; Yoshida, Y.; Akai, S.; Fujioka, H. *Tetrahedron Lett.* **1996**, *37*, 1817−1820. (b) We have already observed that the 2-aryl-2,3-epoxy acylates rearrange via the C2-carbocation intermediates as a result of the stabilization ability of the benzylic cations by aromatic rings, and the methoxy group on the aromatic ring makes the formation of the benzylic cation and the rearrangement reaction faster; see: Kita, Y.; Furukawa, A.; Futamura, J.; Higuchi, K.; Ueda, K.; Fujioka, H. *Tetrahedron Lett.* **2000**, *41*, 2133-2136. (c) Quite recently we found that the reaction of acyclic 2-aryl-2,3-epoxy acylates proceeded via the C3-cleavage of the oxirane ring. However, the intermediates are phenonium ions, which are completely different from the intermediates of eqs 1 and 2 because of the flexibility of the substrates. Kita, Y.; Furukawa, A.; Futamura, J.; Higuchi, K.; Ueda, K.; Fujioka, H. *Tetrahedron* **2001**, *57*, 815−825.

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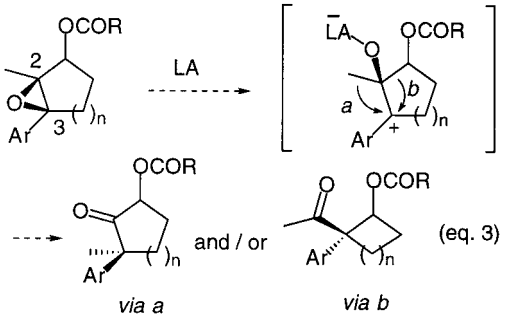
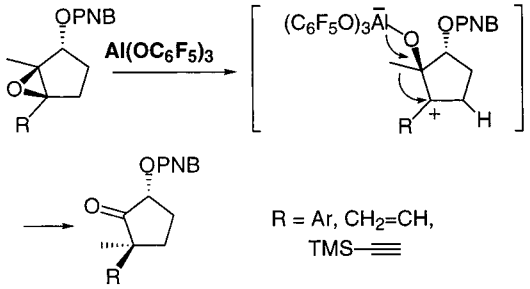
result of the electron-withdrawing nature of the acyloxyalkyl group (eq 1),[4] and (ii) the reactions of cyclic 2-aryl-2,3-epoxy acylates proceed via the C2-cleavage of the oxirane rings (the C2-carbocation intermediates), which show that the aryl group significantly stabilizes the carbocation and overcomes the destabilization ability of the C2-carbocation by the acyloxyalkyl group (eq 2).[5] Therefore, 3-aryl-2,3-epoxy acylates with a C3-aryl group are supposed to rearrange smoothly via the C3-carbocation intermediates by the double regioselective effect of the electron-withdrawing nature of the acyloxyalkyl group and stabilization ability of the phenyl group. We then planned the rearrangement of the 3-aryl-2,3-epoxy acylates in order to construct the chiral quaternary benzylic carbon centers eq 3.[7]



During the study, we determined the importance of the ionic nature of the O−Al bond, the remarkable effect of aluminum reagents, especially $(C_6F_5O)_3Al$, in the reactions of 3-aryl-2,3-epoxy acylates and its generality for the rearrangement of epoxides such as the 3-aryl-, 3-vinyl-, and 3-alkynyl-2,3-epoxy acylates via cation intermediates formed by low activation energy (Scheme 1). We then applied this novel construction method to a chiral benzylic quaternary carbon, leading to the asymmetric synthesis of (*S*)-(+)-sporochnol A (**1**) (Figure 1).

Scheme 1



Results and Discussion

Rearrangements of Epoxy Acylates with C3-Cation Stabilizer. The reaction of *trans*-2,3-epoxy-3-methoxyphenyl-2-methylcyclopentyl *p*-nitrobenzoate **2a**[8]

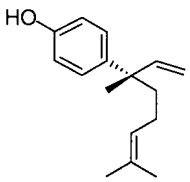
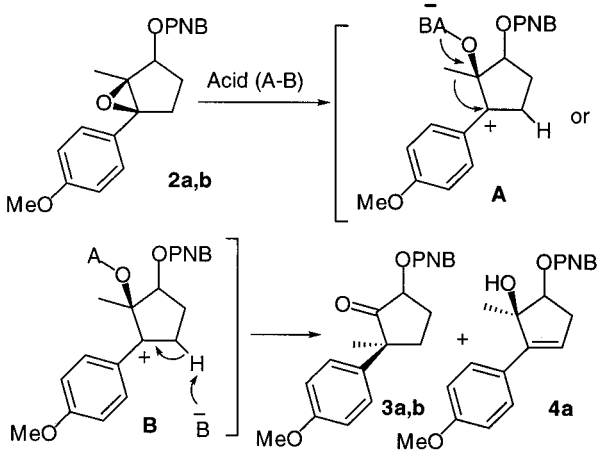


Figure 1. (*S*)-(+)-Sporochnol A (**1**).

with various Lewis acids and organic acids was first examined (Scheme 2). The expected rearranged product **3a**[9] was obtained in 39% by $BF_3{\cdot}Et_2O$ and 25% by $SnCl_4$. *p*-TsOH gave only the allyl alcohol **4a** by hydride elimination from the cation intermediate. Other acids such as CSA, Ph_3CBF_4, $MgBr_2{\cdot}Et_2O$, $(CF_3SO_3)_3Sc$, $(CF_3SO_3)_2Cu$, $(CF_3SO_3)_2Zn$, $(CF_3CO_2)_3Tl$, and $BiCl_3$ also gave **4a** as the major product without the formation of **3a** (by TLC). No reaction occurred using CF_3CO_2Ag or LiCl, and a complex mixture was obtained with TMSOTf (by TLC).

These results are postulated as follows. The reason $BF_3{\cdot}Et_2O$ and $SnCl_4$ give the rearranged product depends on the nature of the oxygen anion. The strong anionic nature of the oxygen atom in the A intermediates would help the rearrangement. On the other hand, the B intermediates, especially formed by organic acids, tend to give the allyl alcohol as a result of the weak anionic nature of the oxygen atom. An increase in the anionic nature of the oxygen atom is necessary to cause the

Scheme 2



trans-isomer **2a**:

$BF_3{\cdot}Et_2O$ (**3a**, 39%), $SnCl_4$ (**3a**, 25%), TsOH (**4a**, quant.), Other acids (**4a**, major product) (see text)

MABR (**3a**, 94%), $Al(OC_6F_5)_3$ (**3a**, 96%), $EtAlCl_2$ (**3a**, 96%)

cis-isomer **2b**:

$BF_3{\cdot}Et_2O$ (**3b**, 66%), $SnCl_4$ (**3b**, 69%),

MABR (**3b**, 96%), $Al(OC_6F_5)_3$ (**3b**, 96%), $EtAlCl_2$ (**3b**, 89%)

(6) For example, see ref 11. For other examples, see: (a) Irie, T.; Suzuki, M.; Kurosawa, E.; Masamune, T. *Tetrahedron* **1970**, *26*, 3271−3277. (b) Ohta, K.; Takagi, M. *Phytochemistry* **1977**, *16*, 1062−1063. (c) Suzuki, M.; Kurosawa, E. *Tetrahedron Lett.* **1978**, 2503−2506. (d) Matsuo, A.; Yuki, S.; Nakayama, M. *Chem. Lett.* **1983**, 1041−1042. (e) Blunt, J. W.; Lake, R. J.; Munro, M. H. G.; *Phytochemistry* **1984**, *23*, 1951−1954. (f) Crews, P.; Selover, S. J. *Phytochemistry* **1986**, *25*, 1847−1852. (g) Matsuo, A.; Yuki, S.; Nakayama, M. *J. Chem. Soc., Perkin Trans. 1* **1986**, 701−710. (h) Kajimoto, T.; Yamashita, M.; Imamura, Y.; Takahasi, K.; Nohara, T.; Shibata, M. *Chem. Lett.* **1989**, 527−530.

(7) For example, the phenyl group stabilizes the benzylic carbocation; see: Ranu, B. C.; Jana, U. *J. Org. Chem.* **1998**, *63*, 8212−8216.

(8) The procedures to prepare the starting epoxy acylates in this manuscript are presented in the Supporting Information.

(9) The relative stereochemistry of **3a,b**, **6a,b**, **3c,d**, and **8a,b** was determined as follows. For example, **3a** and **3b** are diastereomers to each other and show different NMR spectra. The NMR spectrum of **3a** does not contain any peaks of **3b** and the mechanistic consideration helped us to determine the relative stereochemistry of **3a** and **3b**; the starting epoxides **2a** and **2b** have a five-membered ring and the migration of the methyl group occurs on the same side of the five-membered ring. The relative stereochemistries of the other compounds **6a,b**, **3c,d**, and **8a,b** were determined in the same way.

rearrangement reaction from the stable cationic intermediates. If this explanation is correct, the greater ionic nature of the O−A bond in the A intermediates makes the rearrangement more preferable.

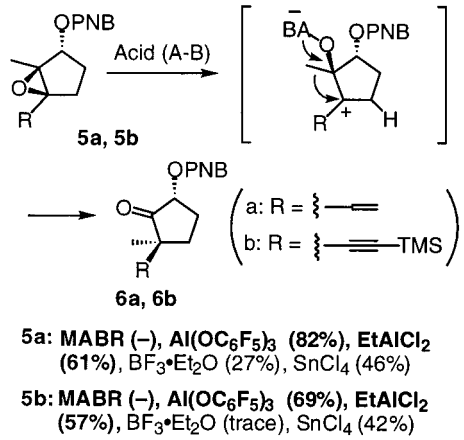
We then examined the bulky Lewis acid, methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR),[10] which has a hard Al metal. The ionic nature of the O−Al bond is high, and its bulkiness would strengthen the migratory aptitude of the neighboring alkyl unit. Although MABR is usually used for the rearrangement of trisubstituted epoxides in the literature because of its bulkiness, we presumed that it would sufficiently work for tetrasubstitued epoxides **2a** because of the easy production of the carbocation intermediates as mentioned above. Indeed, the rearrangement of **2a** proceeded smoothly to give **3a** in 94% yield. MABR is recognized as a special Lewis acid for its bulkiness. At present, it is not clear whether this good result depends on the bulkiness of MABR and/or hardness of the Al metal as mentioned before. Therefore, we next studied other aluminum reagents such as $(C_6F_5O)_3Al$[11] and $EtAlCl_2$ and found that they also work well. The same tendency was observed in the reactions of the *cis*-isomer **2b**, and all of the aluminum reagents gave good results. This means that the bulkiness of the aluminum reagents is not very important for these types of epoxides that produce the cation intermediates with a low activation energy, but the ionic nature of the O−Al bond in the A intermediate is important.

The specificity of the aluminum metal in the reactions of the epoxides having a cation stabilizing group such as a phenyl group via the stable cation intermediates as mentioned above must be due to the strong ionic nature of the oxygen atom of the O−Al bond, which can preferably help the next rearrangement (ionic nature of metal−oxygen bond: B−O 43%; Sn−O 51%; Al−O 63%).[12]

To prove this assumption, we next examined the reactions of the *trans*-2,3-epoxy acylates containing a C3-carbocation stabilizer such as the vinyl or alkynyl groups (**5a** and **5b**). The same tendency as before was observed. For these epoxides, although a complex mixture was obtained by MABR, treatment of $(C_6F_5O)_3Al$ or $EtAlCl_2$ gave the expected results, and the rearranged products **6a** and **6b**[9] were obtained in good yields, respectively. Thus $(C_6F_5O)_3Al$ proved to be the best Lewis acid of choice. For comparison, the results obtained by $BF_3{\cdot}Et_2O$ and $SnCl_4$ are shown together (Scheme 3).

Table 1 shows the results of the reactions of several 2,3-epoxy acylates having a C3-carbocation stabilizer. The *trans*- and *cis*-phenyl substituted compounds **2a**−**f**, two of which, **2e** and **2f**, are six-membered compounds, the *trans*- and *cis*-vinyl and alkynyl compounds **5a,b** and **7a,b** were examined, and $(C_6F_5O)_3Al$ afforded the rearranged products in moderate to good yields in every case.[9] For comparison, the results obtained by $BF_3{\cdot}Et_2O$ and $SnCl_4$ are shown together, and it is revealed that the general superiority of $(C_6F_5O)_3Al$ over other Lewis acids occurs in almost all cases. For **2e** and **2f**, the ring-contracted five-membered products **3e** and **3f** were obtained.[13] The formations of **3e** and **3f** are rationalized as follows. For the *trans*-isomer **2e**, the cation intermediate **i** with one equatorial and three axial substituents first forms and is equilibrated with the more stable intermediate **ii** with one axial and three equatorial substituents because of the flexibility of the six-membered ring and long lifetime of the benzylic carbocation. However, the 1,3-diaxial interaction between the phenyl and OPNB groups in **i** accelerates the rearrangement before reaching sufficient equilibration. The ratio of the products is then different: **3e** (48%) from intermediate **i** and **3f** (18%) from intermediate **ii**. On the other hand, the stabilities of **iii** and **iv** from the *cis*-isomer **2f** are almost the same. Both of them have two equatorial and two axial substituents and no 1,3-diaxial interactions between the substituents. They then reach a sufficient equilibration and rearrange to produce almost the same ratio of products **3e** and **3f** (46% and 40%). (Scheme 4; to clarify the above discussion, the *ent-trans* structure is pictured in Scheme 4).

Scheme 3



5a: MABR (−), $Al(OC_6F_5)_3$ (82%), $EtAlCl_2$ (61%), $BF_3{\cdot}Et_2O$ (27%), $SnCl_4$ (46%)

5b: MABR (−), $Al(OC_6F_5)_3$ (69%), $EtAlCl_2$ (57%), $BF_3{\cdot}Et_2O$ (trace), $SnCl_4$ (42%)

Asymmetric Synthesis of (*S*)-(+)-Sporochnol A. (*S*)-(+)-Sporochnol A (**1**) was isolated from the Caribbean marine alga *Sporochnus bolleanus* by Fenical et al. in 1993 and showed a significant feeding deterrence toward herbivorous fish activity.[14,15]

(10) For preparation, see: Nonoshita, K.; Banno, H.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 316−322. For MABR-promoted epoxide rearrangements, see: (a) Maruoka, K.; Nagahara, S.; Ooi, T.; Yamamoto, H. *Tetrahedron Lett.* **1989**, *30*, 5607−5610. (b) Maruoka, K.; Ooi, T.; Yamamoto, H. *Tetrahedron* **1992**, *48*, 3303−3312. (c) Maruoka, K.; Murase, N.; Bureau, R.; Ooi, T.; Yamamoto, H. *Tetrahedron* **1994**, *50*, 3663−3672. For MABR-promoted rearrangements of epoxy alcohol derivatives, see: (a) Maruoka, K.; Sato, J.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 5449−5480. (b) Maruoka, K.; Sato, J.; Yamamoto, H. *Tetrahedron* **1992**, *48*, 3749−3762.

(11) For synthetic applications of $(C_6F_5O)_3Al$, see: (a) Ishihara, K.; Hanaki, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 7074−7075. (b) Ishihara, K.; Hanaki, N.; Yamamoto, H. *Synlett* **1993**, 127−129.

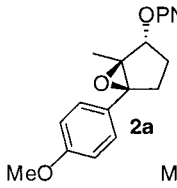
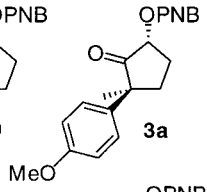
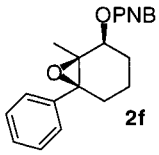
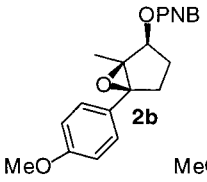
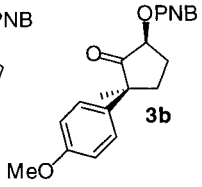
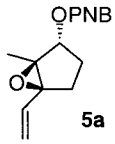
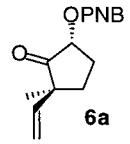
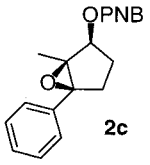
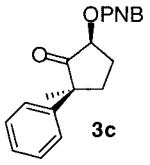
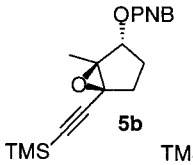
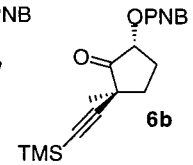
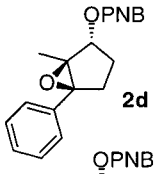
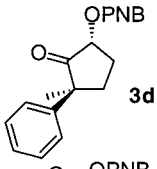
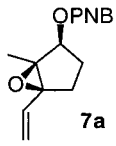
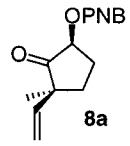
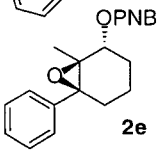
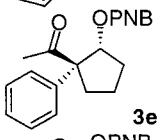
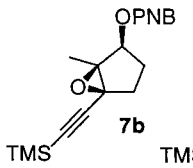
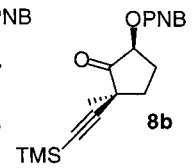
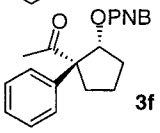
(12) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 3.

(13) Compounds **3e** and **3f** are diastereomers to each other and show different NMR spectra. Compound **3f** is same as compound **5a** in ref 5b or compound **7** in ref 5c (**5a** in ref 5b and **7** in ref 5c are the same compound), whose structure was unambiguously determined by X-ray analysis. The structures of **3e** and **3f** were then determined as shown. The reason for the loss of stereocontrol during this reaction is 1) **2e** and **2f** are six-membered compounds that have conformational flexibility, and 2) the benzylic cation intermediates of **2e** and **2f** have a long lifetime. Although the reaction in ref 5b stereoselectively proceeds, in that case, with the methylene carbon rearranging, it is quite different from this case, where the acyloxymethylene carbon rearranges.

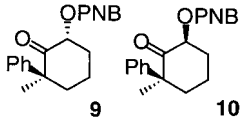
(14) For isolation, structure determination, and biological activity, see: Shen, Y.-C.; Tsai, P. I.; Fenical, W.; Hay, M. E. *Phytochemistry* **1993**, *32*, 71−75.

(15) For the synthesis of natural sporochnol A, see: (a) Kamikubo, T.; Shimizu, M.; Ogasawara, K. *Enantiomer* **1997**, *2*, 297−301. For the synthesis of unnatural sporochnol A, see: (b) Takahashi, M.; Shioura, Y.; Murakami, T.; Ogasawara, K. *Tetrahedoron: Asymmetry* **1997**, *8*, 1235−1242. (c) Fadel, A.; Vandromme, L. *Tetrahedron: Asymmetry* **1999**, *10*, 1153−1162.

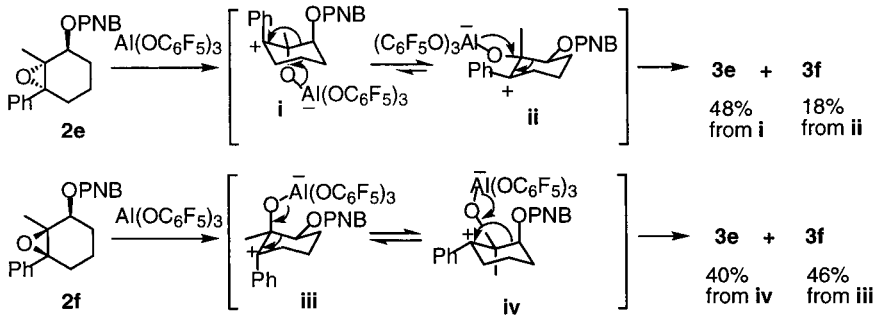
Table 1. Reaction of Various 2,3-Epoxy Acylates with C3-Carbocation Stabilizer and $(C_6F_5O)_3Al$

Substrate	Product	Yield (%)[a]	Substrate	Product	Yield (%)[a]
 **2a**	 **3a**	96 (39, 25)	 **2f**	**3e** + **3f**	40 (11, 7[c]) 46 (15, 32[c])
 **2b**	 **3b**	96 (66, 69)	 **5a**	 **6a**	82 (27, 46)
 **2c**	 **3c**	99 (23, 32)	 **5b**	 **6b**	69 (trace, 42)
 **2d**	 **3d**	95 (53, 88)	 **7a**	 **8a**	94 (0, 42)
 **2e**	 **3e**	48 (34, 27[b])	 **7b**	 **8b**	55 (24, 37)
	 **3f**	+ 18 (19, 21[b])			

[a] Yields in parentheses are the yields obtained by $BF_3{\cdot}Et_2O$ and $SnCl_4$. [b] Another rearranged product **9** was also obtained in 42% yield in addition to **3e** and **3f**. [c] Another rearranged product **10** was also obtained in 23% yield in addition to **3e** and **3f**.


9 **10**

Scheme 4

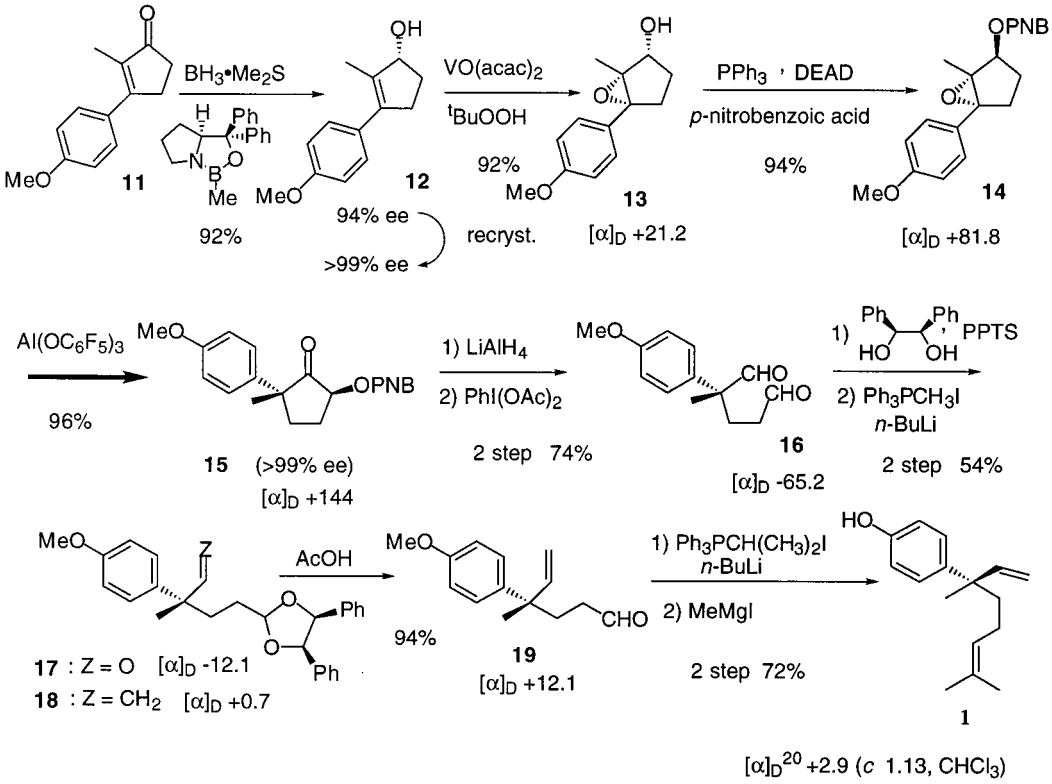


Asymmetric reduction of the enone **11**[16] with Corey's reagent[17] (Scheme 5) gave the optically active allyl alcohol **12** (94% ee), which was recrystallized in hexane to afford the optically pure allyl alcohol (>99% ee, $[\alpha]^{15}_D$ −25.9).[17,18] Stereoselective epoxidation[19] gave the *cis*-epoxy alcohol **13**, which was treated under Mitsunobu's condition[20] with *p*-NO_2-C_6H_4COOH to give the *trans*-epoxy *p*-nitroben-

(16) El-Abbady, A. M.; Doss, S. H. *J. Chem. U. A. R.* **1986**, *11*, 35. Bellina, F.; Ciucci, D.; Rossi, R.; Vergamini, P. *Tetrahedron* **1999**, *55*, 2103−2112.

(17) Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C.-P.; Singh, V. K. *J. Am. Chem. Soc.* **1987**, *109*, 7925−7926. The absolute configuration of the secondary alcohol was deduced by referring to the literature and finally determined by synthesizing the natural (*S*)-(+)-sporochnol A.

Scheme 5



zoate **14**. The $(C_6F_5O)_3Al$ treatment of **14** afforded the rearranged product **15** in 96% yield without loss of chirality.[18] The $LiAlH_4$ reduction of **15** followed by $PhI(OAc)_2$ treatment of the resulting diols (1:1 mixture) gave the dialdehyde **16** in 74% yield. Selective monoacetalization of **16** with *meso*-hydrobenzoin in the presence of 0.1 equiv of PPTS afforded the monoacetal **17**, which was methylenated by the Wittig reaction to give **18** in 54% yield. Deacetalization of **18** by acetic acid gave the olefin aldehyde **19** in 94% yield.[15] The Wittig reaction of the aldehyde **19** with isopropenyl triphenyl phosphine and *n*-BuLi followed by MeMgI treatment of the resulting diolefin by the reported procedure[15] afforded the optically pure (*S*)-(+)-sporochnol A (**1**), whose data (^1H NMR, ^{13}C NMR) were identical with those reported in the literature.[14,15,21]

Conclusion

We found a remarkable effect by aluminum reagents, especially $(C_6F_5O)_3Al$, in the rearrangement reactions of the carbocation stabilizer substituted 2,3-epoxy acylates via the stable carbocation intermediates, whereas the usual Lewis acids such as $BF_3{\cdot}Et_2O$ and $SnCl_4$ do not work well. This will open new directions for the rearrangement reaction of epoxy acylates. Furthermore, we succeeded in applying this method to the synthesis of the optically pure natural sporochnol A in short steps with good yield in each step.

Experimental Section

All melting points are uncorrected. The NMR spectra were measured using 270 or 300 MHz spectrometers with $CDCl_3$ as a solvent and $SiMe_4$ as an internal standard. Infrared (IR) absorption spectra were recorded as a KBr pellet. All solvents were distilled and dried according to standard procedures.

$Al(OC_6F_5)_3$ Treatment of 2,3-Epoxy Acylates (Table 1). *trans*-3-Methyl-3-[4-(methoxy)phenyl]-2-oxacyclopentyl 4-Nitrobenzoate (3a). Me_3Al (*n*-hexane solution, 0.19 mmol) was added dropwise to a solution of C_6F_5OH (105 mg, 0.57 mmol) in dry CH_2Cl_2 (1.9 mL) at ambient temperature under N_2, and the resulting solution was stirred for 1 h. A solution of **2a** (69.7 mg, 0.19 mmol) in dry CH_2Cl_2 (1.1 mL) was added dropwise to the mixture at 0 °C, and the solution was stirred for 15 min at the same temperature. After completion of the reaction (checked by TLC), the reaction mixture was quenched by aqueous oxalic acid and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by SiO_2 column chromatography using hexane−AcOEt (3/1) as the eluent to give **3a** (67.0 mg, 96%). Light yellowish crystals; mp 145−147 °C (hexane−AcOEt); IR (KBr) 1755, 1732, 1532, 1267 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (s, 3H), 2.08−2.58 (m, 4H), 3.80 (s, 3H), 5.53 (t, 1H, J = 9.5 Hz), 6.89 (d, 2H, J = 8.5 Hz), 7.29 (d, 2H, J = 8.5 Hz), 8.26 (d, 2H, J = 9.0 Hz), 8.31 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 25.0, 26.3, 33.1, 49.9, 55.3, 76.8, 114.1, 123.5, 126.9, 131.0, 134.7, 134.8, 150.7, 158.5, 163.9, 212.7. Anal. Calcd for $C_{20}H_{19}NO_6$: C, 65.03; H, 5.19; N, 3.79; O, 25.99. Found: C, 64.99; H, 5.31; N, 3.75; O, 25.95.

***cis*-3-Methyl-3-[4-(methoxy)phenyl]-2-oxacyclopentyl 4-Nitrobenzoate (3b).** By the same procedure as for **3a**, **3b** (40.1 mg, 95%) was obtained from **2b** (42.1 mg, 0.11 mmol), $Al(OC_6F_5)_3$ (0.12 mmol prepared from 0.12 mmol of Me_3Al and

(18) The ee values of all the optically active compounds were determined by HPLC analysis. (For the allyl alcohol **12**: CHIRALCEL OD; hexane/*i*-PrOH = 99/1; flow rate 1.0 mL/min. For **15**: CHIRALCEL OD; hexane/*i*-PrOH = 80/20; flow rate 1.0 mL/min).

(19) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136−6137.

(20) Mitsunobu, O.; Kimura, J.; Iizumi, K.; Yanagida, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 510−513.

(21) Optical rotation of the synthetic (*S*)-(+)-sporochnol A (**1**) {$[\alpha]^{20}_D$ +2.0 (*c* 1.13, $CHCl_3$)} is different from the reported values {$[\alpha]_D^{30}$ +2.8 (*c* 0.9, $CHCl_3$)[15a] and $[\alpha]_D$ +10.0 (*c* 1.0, $CHCl_3$)[14]}, both of which are also different from each other. The optical purity of the synthetic (*S*)-(+)-sporochnol A (>99% ee) was determined by HPLC analysis (CHIRALCEL; hexane/*i*-PrOH = 95/5; flow rate 1.0 mL/min).

0.36 mmol of C_6F_5OH), and CH_2Cl_2 (1.2 mL, 1 mL). The eluent for SiO_2 column chromatography was hexane−AcOEt (3/1). Yellowish oil; IR (KBr) 1755, 1732, 1532, 1296 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.49 (s, 3H), 1.91−2.05 (m, 2H), 2.54−2.59 (m, 1H), 2.71−2.74 (m, 1H), 3.81 (s, 3H), 5.49−5.55 (m, 1H), 6.91 (d, 2H, J = 8.9 Hz), 7.32 (d, 2H, J = 8.9 Hz), 8.17 (d, 2H, J = 8.9 Hz), 8.27 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 26.3, 26.6, 33.0, 51.0, 55.2, 75.8, 114.1, 123.5, 127.4, 131.0, 133.2, 134.7, 150.7, 158.5, 163.9, 213.4. Anal. Calcd for $C_{20}H_{19}NO_6$: C, 65.03; H, 5.19; N, 3.79; O, 25.99. Found: C, 64.81; H, 5.21; N, 3.78; O, 26.2.

***cis*-3-Methyl-2-oxo-3-phenylcyclopentyl 4-Nitrobenzoate (3c).** By the same procedure as for **3a**, **3c** (49.9 mg, 99%) was obtained from **2c** (50.4 mg, 0.15 mmol), $Al(OC_6F_5)_3$ (0.150 mmol prepared from 0.15 mmol of Me_3Al and 0.45 mmol of C_6F_5OH), and CH_2Cl_2 (1.5 mL, 1 mL). The eluent for SiO_2 column chromatography was hexane−AcOEt (5/1). Light yellowish oil; IR (KBr) 1755, 1732, 1539, 1267, 1123, 1107 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.52 (s, 3H), 1.91−2.08 (m, 2H), 2.55−2.78 (m, 2H), 5.53 (dd, 1H, J = 10.1, 8.2 Hz), 7.27−7.42 (m, 5H), 8.17 (d, 2H, J = 9.2 Hz), 8.26 (d, 2H, J = 9.2 Hz); ^{13}C NMR ($CDCl_3$) δ 26.3, 26.5, 33.1, 51.8, 75.8, 123.5, 126.3, 127.1, 128.8, 131.0, 134.8, 141.6, 150.7, 164.0, 213.5. Anal. Calcd for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13; O, 23.58. Found: C, 67.05; H, 5.14; N, 4.04; O, 23.77.

***trans*-3-Methyl-2-oxo-3-phenylcyclopentyl 4-Nitrobenzoate (3d).** By the same procedure as for **3a**, **3d** (47.7 mg, 95%) was obtained from **2d** (50.2 mg, 0.15 mmol), $Al(OC_6F_5)_3$ (0.150 mmol prepared from 0.15 mmol of Me_3Al and 0.45 mmol of C_6F_5OH), and CH_2Cl_2 (1.5 mL, 1 mL). The eluent for SiO_2 column chromatography was hexane−AcOEt (5/1). Light yellowish crystals; mp 102−104 °C (hexane−AcOEt); IR (KBr) 1755, 1732, 1532, 1267, 1134 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53 (s, 3H), 2.11−2.59 (m, 4H), 5.55 (dd, 1H, J = 10.0, 8.5 Hz), 7.26−7.40 (m, 5H), 8.27 (d, 2H, J = 8.9 Hz), 8.32 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 25.0, 26.3, 33.0, 50.5, 76.9, 123.5, 125.7, 127.0, 128.8, 131.0, 134.8, 142.9, 150.7, 163.8, 212.5. Anal. Calcd for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13; O, 23.58. Found: C, 67.05; H, 5.14; N, 4.04; O, 23.71.

***trans*-2-Acetyl-2-phenylcyclopentyl 4-Nitrobenzoate (3e) and *cis*-2-Acetyl-2-phenylcyclopentyl 4-Nitrobenzoate (3f).** From **2e**: by the same procedure as for **3a**, **3e** (47.8 mg, 48%) and **3f** (18.0 mg, 18%) were obtained from **2e** (100 mg, 0.283 mmol), $Al(OC_6F_5)_3$ (0.283 mmol prepared from 0.283 mmol of Me_3Al and 0.85 mmol of C_6F_5OH), and CH_2Cl_2 (1.8 mL, 1 mL). The eluent for SiO_2 column chromatography was hexane−AcOEt (10/1). From **2f**: by the same procedure as for **3a**, **3e** (39.8 mg, 40%) and **3f** (46.3 mg, 46%) were obtained from **2f** (100 mg, 0.283 mmol), $Al(OC_6F_5)_3$ (0.283 mmol prepared from 0.283 mmol of Me_3Al and 0.85 mmol of C_6F_5OH)), and CH_2Cl_2 (1.8 mL, 1 mL). **Data for 3e:** colorless crystals; mp 149−151 °C (hexane−AcOEt); IR (KBr) 1725, 1705, 1532, 1275, 1121, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62−2.05 (m, 3H), 1.99 (s, 3H), 2.39−2.59 (m, 3H), 6.21 (d, 1H, J = 5.5 Hz), 7.21−7.32 (m, 5H), 7.63 (d, 2H, J = 8.9 Hz), 8.09 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 21.5, 25.2, 31.5, 69.6, 79.9, 123.3, 127.5, 127.6, 128.8, 130.2, 135.8, 137.5, 150.2, 163.8, 207.5. Anal. Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96; O, 22.64. Found: C, 67.83; H, 5.44; N, 3.97; O, 22.76. **Data for 3f:** colorless needles; mp 149−151 °C (hexane−AcOEt); IR (KBr) 1725, 1715, 1530, 1277 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.57−1.62 (m, 1H), 1.86−1.98 (m, 2H), 1.91 (s, 3H), 2.20−2.37 (m, 2H), 2.71−2.83 (m, 1H), 6.17 (d, 1H, J = 5.2 Hz), 7.30−7.43 (m, 5H), 8.14 (d, 2H, J = 9.1 Hz), 8.30 (d, 2H, J = 9.1 Hz); ^{13}C NMR ($CDCl_3$) δ 20.6, 27.3, 31.6, 33.2, 68.5, 81.2, 123.7, 126.3, 127.7, 129.2, 130.7, 135.3, 138.8, 150.7, 163.9, 205.7. Anal. Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96; O, 22.64. Found: C, 67.83; H, 5.44; N, 3.97; O, 22.66.

***trans*-3-Methyl-2-oxo-3-vinylcyclopentyl 4-Nitrobenzoate (6a).** By the same procedure as for **3a**, **6a** (82.4 mg, 82%) was obtained from **5a** (100 mg, 0.346 mmol), $Al(OC_6F_5)_3$ (0.35 mmol prepared from 0.35 mmol of Me_3Al and 1.05 mmol of C_6F_5OH), and CH_2Cl_2 (2.5 mL, 1 mL). The eluent for SiO_2 column chromatography was hexane−AcOEt (10/1). White crystals; mp 107−109 °C (hexane−AcOEt); IR (KBr) 1755, 1728, 1522 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 3H), 2.01−2.18 (m, 3H), 2.51−2.59 (m, 1H), 5.15 (d, 1H, J = 17.0 Hz), 5.17 (d, 1H, J = 11.0 Hz), 5.46 (t, 1H, J = 9.0 Hz), 5.89 (dd, 1H, J = 11.0, 17.0 Hz), 8.23−8.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 23.5, 25.0, 30.8, 49.8, 76.3, 114.6, 123.5, 131.0, 134.8, 140.2, 150.7, 163.8. Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84; O, 27.65. Found: C, 62.21; H, 5.26; N, 4.85; O, 27.68.

***trans*-3-Methyl-2-oxo-3-(trimethylsilylethynyl)cyclopentyl 4-Nitrobenzoate (6b).** By the same procedure as for **3a**, **6b** (42.0 mg, 69%) was obtained from **5b** (60.4 mg, 0.168 mmol), $Al(OC_6F_5)_3$ (0.168 mmol prepared from 0.168 mmol of Me_3Al and 0.504 mmol of C_6F_5OH), and CH_2Cl_2 (0.7 mL, 1 mL). The eluent for SiO_2 column chromatography was hexane−AcOEt (15/1). White crystals; mp 99−101 °C; IR (KBr) 2164, 1769, 1732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.43 (s, 3H), 1.95−2.02 (m, 1H), 2.14−2.21 (m, 1H), 2.28−2.34 (m, 1H), 2.58−2.60 (m, 1H), 5.63 (t, 1H, J = 9.0 Hz), 8.22 (d, 2H, J = 8.7 Hz), 8.29 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 0.37, 23.6, 25.0, 34.2, 42.4, 75.5, 88.1, 105.8, 123.6, 131.1, 134.7, 150.8, 163.8, 207.7. Anal. Calcd for $C_{18}H_{21}NO_5Si$: C, 60.14; H, 5.89; N, 3.90; O, 22.26; Si; 7.81. Found: C, 59.98; H, 5.93; N, 3.89; O, 22.16; Si, 8.04.

***cis*-3-Methyl-2-oxo-3-vinylcyclopentyl 4-Nitrobenzoate (8a).** By the same procedure as for **3a**, **8a** (94.1 mg, 94%) was obtained from **7a** (100 mg, 0.346 mmol) and $Al(OC_6F_5)_3$ (0.350 mmol prepared from 0.350 mmol of Me_3Al and 1.05 mmol of C_6F_5OH), and CH_2Cl_2 (2.5 mL, 1 mL). The eluent for SiO_2 column chromatography was hexane−AcOEt (10/1). Light yellowish crystals; mp 78−81 °C (hexane−AcOEt); IR (KBr) 1755, 1732, 1532 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (s, 3H), 1.76−1.88 (m, 1H), 1.93−2.08 (m, 1H), 2.28−2.36 (m, 1H), 2.48−2.57 (m, 1H), 5.15 (d, 1H, J = 18.0 Hz), 5.21 (d, 1H, J = 11.0 Hz), 5.45 (dd, 1H. J = 8.0, 11.0 Hz), 5.79 (dd, 1H, J = 11.0, 18.0 Hz), 8.24 (d, 2H, J = 8.5 Hz), 8.30 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 23.7, 25.8, 31.1, 50.3, 75.9, 115.1, 123.5, 131.0, 134.8, 139.5, 150.7, 163.9, 212.6. Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.28; H, 5.23; N, 4.84; O, 27.65. Found: C, 62.21; H, 5.26; N, 4.85; O, 27.88.

***cis*-3-Methyl-2-oxo-3-(trimethylsilylethynyl)cyclopentyl 4-Nitrobenzoate (8b).** By the same procedure as for **3a**, **8b** (29.3 mg, 55%) was obtained from **7b** (53.1 mg, 0.148 mmol), $Al(OC_6F_5)_3$ (0.148 mmol prepared from 0.15 mmol of Me_3Al and 0.444 mmol of C_6F_5OH), and CH_2Cl_2 (0.8 mL, 0.7 mL). The eluent for SiO_2 column chromatography was benzene−AcOEt (3/1). White crystals; mp 146−148 °C; IR (KBr) 2161, 1765, 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 9H), 1.43 (s, 3H), 1.77−1.85 (m, 1H), 2.20−2.60 (m, 1H), 2.43−2.55 (m, 2H), 5.44 (dd, 1H, J = 8.0, 11.0 Hz), 8.25 (d, 2H, J = 9.0 Hz), 8.31 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ −0.1, 23.2, 26.3, 34.0, 43.6, 75.1, 88.0, 105.3, 123.5, 131.1, 134.7, 150.8, 163.9, 207.7. Anal. Calcd for $C_{18}H_{21}NO_5Si$: C, 60.14; H, 5.89; N, 3.90; O, 22.26; Si; 7.81. Found: C, 59.99; H, 5.88; N, 3.88; O, 22.20; Si, 8.05.

Synthesis of (*S*)-(+)-Sporochnol A (1) (Scheme 5). (−)-(1*R*)-2-Methyl-3-[4-(methoxy)phenyl]cyclopent-2-ene-1-ol (12). BH_3•Me_2S (2 M in THF, 3.1 mL, 6.20 mmol) was added dropwise to a solution of (*S*)-5,5-diphenyl-2-methyl-3,4-propan-1,3,2-oxazaborolidine (1.72 g, 6.21 mmol) in THF (40 mL) at 0 °C under N_2. After 30 min of stirring, a solution of the enone **11** (1.26 g, 6.23 mmol) in THF (20 mL) was added slowly to the resulting mixture. After 30 min of stirring, MeOH was added to the mixture. The solvent was removed in vacuo. The residue was purified by SiO_2 column chromatography using hexane−AcOEt (2/1) as the eluent to give **12** (1.28 g, 92%; HPLC analysis 94% ee by CHIRALCEL OD, hexane/*i*-PrOH = 99/1, flow rate 1.0 mL/min), which was recrystalized in hexane to give optically pure **12** (731 mg, 59%). Light yellowish crystals; mp 66−68 °C (hexane−AcOEt); IR (KBr) 3400−3200, 1514, 1248, 1036 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68−1.79 (m, 1H), 1.74 (s, 1H), 1.91 (s, 3H), 2.32−2.44 (m, 1H), 2.61−2.80 (m, 2H), 3.81 (s, 3H), 4.72 (brs, 1H), 6.89 (d, 2H, J = 8.9 Hz), 7.26 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 12.9, 32.6, 33.9, 55.2, 82.2, 113.5, 128.9, 130.3, 134.9, 137.5, 158.4; $[\alpha]^{15}_D$ −25.9 (*c* 1.05, $CHCl_3$); HPLC analysis >99% ee (CHIRALCEL OD; hexane/*i*-PrOH = 99/1; flow rate 1.0 mL/min; t_R 84.3

min for optically pure **12**, 80.3 and 85.9 min for the racemic one). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; O, 15.67. Found: C, 76.49; H, 7.85; O, 15.66.

(+)-(1*R*,2*R*,5*R*)-1-Methyl-5-[4-(methoxy)phenyl]-6-oxabicyclo[3.1.0]hexane-2-ol (13). A solution of *t*-BuOOH (dried over $MgSO_4$ before use, 68%, 1.40 g, 10.6 mmol) in benzene (10 mL) was added dropwise to a solution of **12** (726 mg, 3.55 mmol) and 0.1 equiv of $VO(acac)_2$ in benzene (20 mL) at room temperature under N_2. After 1 h of stirring at room temperature, saturated aqueous $Na_2S_2O_3$ was added to the mixture. The resulting solution was extracted with AcOEt. The organic layer was washed with water and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by SiO_2 column chromatography using hexane−AcOEt (1/1) as the eluent to give **13** (721 mg, 92%). Colorless needles, mp 102−103 °C (hexane−AcOEt); IR (KBr) 3500−3300, 1520, 1248 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.33−1.45 (m, 1H), 1.99−2.17 (m, 4H), 3.81 (s, 3H), 4.11−4.17 (m, 1H), 6.90 (d, 2H, J = 8.9 Hz), 7.26 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 12.1, 28.4, 29.2, 55.3, 70.6, 71.3, 76.4, 113.7, 127.5, 128.6, 159.1; $[\alpha]^{22}_D$ +21.2 (*c* 1.29, $CHCl_3$). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32; O, 21.79. Found: C, 70.96; H, 7.33; O, 21.71.

(+)-(1*R*,2*S*,5*R*)-1-Methyl-5-[4-(methoxy)phenyl]-6-oxabicyclo[3.1.0]hex-2-yl 4-Nitrobenzoate (14). *p*-Nitrobenzoic acid (1.06 g, 6.34 mmol) and Ph_3P (1.65 g, 6.29 mmol) were added to a solution of **13** (691 mg, 3.14 mmol) in toluene (20 mL) at 0 °C under N_2. Diethyl azodicarboxylate (toluene solu., 2.70 mL, 6.20 mmol) was added dropwise to the resulting solution. The mixture was stirred for 0.5 h and then treated with saturated aqueous $NaHCO_3$. The resulting solution was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by SiO_2 column chromatography using hexane−AcOEt (6/1) as the eluent to give *trans*-epoxy *p*-nitrobenzoate (+)-**14** (1.08 g, 94%, HPLC analysis >99% ee (CHIRALCEL OD; hexane/*i*-PrOH = 97/3; flow rate 1.0 mL/min; t_R 34.3 min for optically pure **14**, 35.3 and 38.4 min for the racemic one)). Light yellowish crystals; mp 103−105 °C (hexane−AcOEt); IR (KBr) 1728, 1532, 1273, 1248, 1117, 1103 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.83−2.25 (m, 3H), 2.46−2.54 (m, 1H), 3.83 (s, 3H), 5.56 (d, 1H, J = 5.5 Hz), 6.94 (d, 2H, J = 8.5 Hz), 7.36 (d, 2H, J = 8.5 Hz), 8.21 (d, 2H, J = 8.9 Hz), 8.32 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 11.4, 27.4, 30.2, 55.3, 69.1, 72.0, 79.2, 113.8, 123.6, 127.6, 130.7, 135.4, 150.6, 159.2, 163.9; $[\alpha]^{21}_D$ +81.8 (*c* 1.08, $CHCl_3$). Anal. Calcd for $C_{20}H_{19}NO_6$: C, 65.03; H, 5.19; N, 3.79; O, 25.99. Found: C, 64.93; H, 5.23; N, 3.75; O, 26.09.

(+)-(1*S*,3*R*)-3-Methyl-3-[4-(methoxy)phenyl]-2-oxacyclopentyl 4-Nitrobenzoate (15). Trimethylaluminum (0.98 M in *n*-hexane, 1.40 mL, 1.37 mmol) was added dropwise to a solution of pentafluorophenol (777 mg, 4.2 mmol) in dry CH_2Cl_2 (14 mL) under Ar at ambient temperature, and the reaction mixture was stirred for an additional 1 h. A solution of **14** (501 mg, 1.37 mmol) in CH_2Cl_2 (14 mL) was added to the mixture cooled to 0 °C, and the solution was stirred for 15 min at the same temperature. The reaction mixture was quenched by 1 N HCl, and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by SiO_2 column chromatography using hexane−AcOEt (3/1) as the eluent to give **15** (471 mg, 94%, HPLC analysis >99% ee (CHIRALCEL OD; hexane/*i*-PrOH = 80/20; flow rate 1.0 mL/min; t_R 44.6 min for optically pure **15**, 44.3 and 82.0 min for the racemic one)). Light yellowish crystals; mp 145−147 °C (hexane−AcOEt); IR (KBr) 1755, 1732, 1532, 1267 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (s, 3H), 2.08−2.58 (m, 4H), 3.80 (s, 3H), 5.53 (t, 1H, J = 9.5 Hz), 6.89 (d, 2H, J = 8.5 Hz), 7.29 (d, 2H, J = 8.5 Hz), 8.26 (d, 2H, J = 9.0 Hz), 8.31 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 25.0, 26.3, 33.1, 49.9, 55.3, 76.8, 114.1, 123.5, 126.9, 131.0, 134.7, 134.8, 150.7, 158.5, 163.9, 212.7; $[\alpha]^{22}_D$ +144 (*c* 1.25, $CHCl_3$). Anal. Calcd for $C_{20}H_{19}NO_6$: C, 65.03; H, 5.19; N, 3.79; O, 25.99. Found: C, 64.99; H, 5.31; N, 3.75; O, 25.95.

(−)-(2*R*)-2-Methyl-2-[4-(methoxy)phenyl]pentane-1,5-dial (16). A solution of **15** (199 mg, 0.539 mmol) in freshly distilled THF (3 mL) was added dropwise to a suspension of lithium aluminum hydride (51.6 mg, 1.08 mmol) in freshly distilled THF (3 mL) under N_2 at 0 °C, and the reaction mixture was stirred for an additional 1.5 h. The mixture was quenched by water and extracted with ether. The organic layer was washed with saturated aqueous Rochelle salt and brine and dried over Na_2SO_4. The solution was filtered through Celite pad. After concentration in vacuo, crude diol was obtained. The diol was dissolved in dry CH_2Cl_2 (6 mL), and $PhI(OAc)_2$ (354 mg, 1.10 mg) was charged into the solution at 0 °C under N_2. After 4 h of stirring, saturated aqueous $NaHCO_3$ was charged into the mixture, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by SiO_2 column chromatography using benzene−AcOEt (7/1) as the eluent to give **16** (88.4 mg, 2 steps 74%). Light yellowish oil; IR (KBr) 1725, 1514, 1256 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (s, 3H), 2.08−2.37 (m, 4H), 3.81 (s, 3H), 6.92 (d, 2H, J = 8.9 Hz), 7.15 (d, 2H, J = 8.9 Hz), 9.44 (s, 1H), 9.67 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.7, 28.1, 39.0, 52.4, 55.3, 114.5, 128.3, 130.4, 159.0, 201.4; $[\alpha]^{20}_D$ −65.2 (*c* 1.45, $CHCl_3$). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32; O, 21.79. Found: C, 70.56; H, 7.33; O, 22.11.

(−)-(2*R*)-4-(4,5-Diphenyl-1,3-dioxolan-2-yl)-2-methyl-2-[4-(methoxy)phenyl]-butanal (17). Pyridinium *p*-toluenesulfonate (38.7 mg, 0.153 mmol) and *meso*-hydrobenzoin (408 mg, 1.90 mmol) were added to a solution of **16** (209 mg, 0.949 mmol) in dry toluene (9.5 mL) under N_2. The mixture was stirred at 70 °C for 9 h. After potassium carbonate was charged into the mixture, it was stirred for several minutes, and the resulting mixture was washed with saturated aqueous $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by SiO_2 column chromatography using hexane−AcOEt (4/1) as an eluent to give **17** (269 mg, 68%). Colorless oil. IR (KBr) 1723, 1514, 1254, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53 (s, 3H), 1.82−2.36 (m, 4H), 3.81 (s, 3H), 5.20 (t, 1H, J = 5.0 Hz), 5.31 (s, 2H), 6.90−7.26 (m, 14H), 9.51 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.8, 28.4, 30.4, 52.9, 55.3, 82.2, 82.4, 104.2, 114.4, 126.8, 126.9, 127.2, 127.3, 127.4, 127.5, 128.4, 131.0, 137.1, 137.3, 158.8, 201.9; $[\alpha]^{22}_D$ −12.1 (*c* 1.24, $CHCl_3$); HRMS (FAB) calcd for $C_{27}H_{29}O_4$ (M^+ + H) 418.2099, found 418.2118. Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78; O, 15.36. Found: C, 77.51; H, 6.86; O, 15.63.

(+)-(3*S*)-3-Methyl-3-[4-(Methoxy)phenyl]pent-4-enyl-4,5-diphenyl-1,3-dioxolane (18). *n*-BuLi (*n*-hexane solution, 190 μL, 0.285 mmol) was added dropwise to a solution of methyltriphenylphosphonium iodide (128.4 mg, 0.318 mmol) in freshly distilled THF (1 mL) at 0 °C under N_2, and the mixture was stirred for 1 h at the same temperature. A solution of **17** (37.1 mg, 0.089 mmol) in freshly distilled THF (1.5 mL) was charged into the solution at 0 °C, and the mixture was stirred for additional 1.5 h. The resulting solution was quenched with saturated aqueous NH_4Cl and extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by SiO_2 column chromatography using hexane−AcOEt (7/1) as the eluent to give **18** (32.7 mg, 88%). Colorless oil; IR (KBr) 1512, 1250, 1136, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (s, 3H), 1.86−2.14 (m, 4H), 3.80 (s, 3H), 5.08−5.20 (m, 3H), 5.29 (s, 2H), 6.06 (dd, 1H, J = 17.4, 11.0 Hz), 6.87 (d, 2H, J = 9.0 Hz), 6.93−7.24 (m, 10H), 7.30 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 25.2, 29.1, 35.3, 43.4, 55.2, 82.2, 82.3, 104.7, 111.9, 113.5, 126.8, 126.9, 127.1, 127.2, 127.5, 127.7, 137.2, 137.3, 138.9, 146.8, 157.7; $[\alpha]_D^{20}$ +0.7 (*c* 1.11, $CHCl_3$); HRMS (FAB) calcd for $C_{28}H_{31}O_3$ (M^+ + H) 415.2273, found 415.2274. Anal. Calcd for $C_{28}H_{30}O_3$: C, 81.13; H, 7.29; O, 11.58. Found: C, 80.92; H, 7.35; O, 11.73.

(+)-(4*S*)-4-Methyl-4-[4-(Methoxy)phenyl]hex-5-enal (19). Compound **18** (40.7 mg, 0.098 mmol) was dissolved in 80% aqueous acetic acid (4 mL), and the solution was refluxed for 1 h. The reaction mixture was neutralized by 2 N NaOH and extracted with ether. The organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by SiO_2 column chromatography using hexane−AcOEt (5/1) as the eluent to give **19** (20.1 mg, 94%).

Colorless oil; IR (KBr) 1725, 1514, 1252 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 3H), 1.97−2.36 (m, 4H), 3.79 (s, 3H), 5.06 (d, 1H, J = 17.4 Hz), 5.13 (d, 1H, J = 10.7 Hz), 5.97 (dd, 1H, J = 17.4, 10.7 Hz), 6.85 (d, 2H, J = 8.9 Hz), 7.21 (d, 2H, J = 8.9 Hz), 9.67 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.1, 32.5, 39.9, 43.0, 55.2, 112.3, 113.6, 127.6, 138.2, 146.2, 157.9, 202.3; $[\alpha]^{18}_D$ +12.1 (*c* 1.32, $CHCl_3$). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31; O, 14.66. Found: C, 77.00; H, 8.40; O, 14.60.

(*S*)-(+)-Sporochnol A (1). *n*-BuLi (*n*-hexane solution, 1.00 mL, 1.50 mmol) was added dropwise to a solution of isopropyltriphenylphosphonium iodide (684 mg, 1.58 mmol) in freshly distilled THF (8 mL) at 0 °C under N_2. The mixture was stirred for 1 h at the same temperature. A solution of **19** (64.9 mg, 0.298 mmol) in freshly distilled THF (8 mL) was charged into the solution at 0 °C, and the resulting solution was stirred for an additional 1 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. The residue on filtration through Celite pad yielded crude *O*-methyl sporochnol A. Methylmagnesium iodide (ether solution, 7.10 mL, 5.96 mmol) was added to the solution of the crude *O*-methyl sporochnol A at 0 °C under N_2, and the solution was concentrated in vacuo. The mixture was heated to 180 °C, stirred for 20 min, diluted with ether, and then quenched with saturated aqueous NH_4Cl. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by SiO_2 column chromatography using hexane−AcOEt (6/1) as the eluent to give (*S*)-(+)-sporochnol A (**1**). Colorless oil; IR (KBr) 3400−3200, 1512, 1441, 1375, 1236, 1178 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (s, 3H), 1.51 (s, 3H), 1.66 (s, 3H), 1.67−1.86 (m, 4H), 4.65 (br s, 1H), 4.98−5.09 (m, 3H), 5.99 (dd, 1H, J = 17.4, 10.7 Hz), 6.76 (d, 2H, J = 8.9 Hz), 7.18 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 17.6, 23.3, 25.0, 25.7, 41.2, 43.7, 111.5, 114.8, 124.7, 127.8, 131.3, 139.7, 147.2, 153.4; $[\alpha]^{20}_D$ +2.0 (*c* 1.13, $CHCl_3$); HPLC analysis >99% ee (CHIRALCEL OD; hexane/*i*-PrOH = 95/5; flow rate 1.0 mL/min; t_R 18.69 min for optically pure **1**, 19.88 and 31.68 min for the racemic one).

Supporting Information Available: Experimental procedures for the syntheses of the epoxy acylates **2a**−**f**, **5a,b**, and **7a,b** with spectroscopic and analytical data and acid treatment of epoxy acylates including the spectroscopic and analytical data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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