# Acid-Promoted Rearrangement of Cyclic α,β-Epoxy Acylates: Stereoselective Synthesis of Spirocyclanes and Quaternary Carbon Centers

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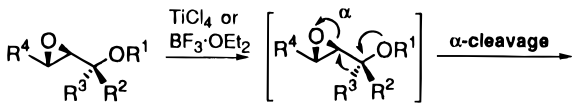
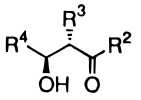
The rearrangement reaction of α,β-epoxy acylates in cyclic systems was studied. The treatment of *cis*-derivatives with a Lewis acid afforded rearranged products *via* the regioselective β-cleavage of the oxirane ring due to the electron-withdrawing nature of the acyloxy group, whereas *trans*-derivatives enhanced the neighboring group participation to yield only a small amount of rearranged products. This rearrangement reaction proved to be useful for the construction of a variety of spirocyclane systems or quaternary carbon centers on rings and could be applied to their syntheses as optically active forms.

Several rearrangement reactions of α,β-epoxy alcohols and their silyl ethers, which could be easily prepared as the optically active form, have been developed in the last decade. These reactions are very useful as one of the stereoselective synthetic methods of optically active carbonyl compounds. In these cases, when the epoxides are equally substituted, the cleavage of the oxirane ring mainly occurred at the α-position proximate to the alcohol moieties because of their electron-donating nature, and then successive rearrangement afforded β-hydroxy carbonyl compounds (eq 1).[1]

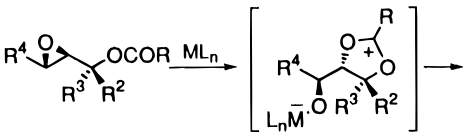



$R^1$=$SiR_3$, H ($R^2$,$R^3$= alkyl, aryl, alkenyl; $R^4$= H, alkyl)

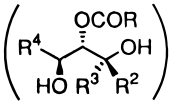


(eq 1)

On the other hand, there have been few examples[2] using epoxy acylates due to the ring opening nature of the epoxide, which is assisted by the acyloxy group, to form the dioxenium ion (eq 2).[3] However it appeared to us that a new type of rearrangement proceeds by selective

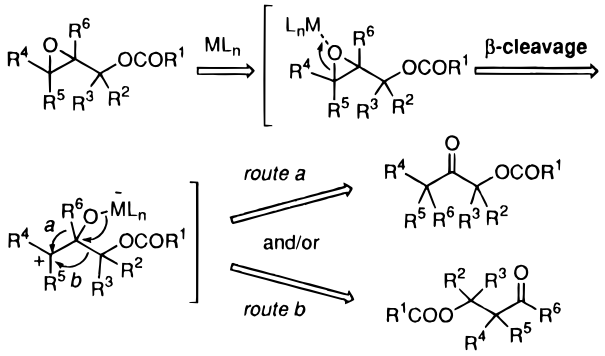



no rearrangement product



(eq 2)

**Scheme 1**




cleavage of the epoxide at the β-position promoted by the electron-withdrawing nature of the acyloxy group, in other words, by destabilization of the cation at the α-position due to the electron deficiency of the acyloxylated carbon, if such a neighboring group participation is suppressed (Scheme 1). According to this idea, we have recently reported that the treatment of *cis*-α,β-epoxy acylates in bicyclo[*n*.3.0]alkane systems with $BF_3$·$OEt_2$ afforded 2-(acyloxy)-1-oxospiro[4.*n*]alkanes by regio- and stereoselective rearrangement, and that this reaction could be applied to the synthesis of optically active spiro compounds.[4] We also found that the rearrangement reaction could be applied to monocyclic systems to stereoselectively give the quaternary carbon centers. In this paper, we describe the full details of our work connected with the rearrangement reaction of *cis*-α,β-epoxy acylates in cyclic systems.

**Rearrangement Reaction in Bicyclic Systems: Synthesis of Spirocyclanes.** Chiral spirocyclane systems are found in many biologically active natural products such as spiro[4.5]decane sesquiterpenes,[5] ginkgolide,[6] etc. Although many methodologies for constructing them have been developed so far,[7] there are only a few ways applicable to the synthesis of optically

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

(1) For examples of electron-donating hydroxy derivatives initiating cleavage of the oxirane ring at the α-position of the hydroxy function and successive migration, see: Maruoka, K.; Sato, J.; Yamamoto, H. *Tetrahedron* **1992**, *48*, 3749. Nagasawa, T.; Taya, K.; Kitamura, M. Suzuki, K. *J. Am. Chem. Soc.* **1996**, *118*, 8949 and references cited therein. Rearrangement of epoxy alcohol derivative, see: Marson, C. M.; Walker, A. J.; Pickering, J.; Hobson A. D.; Wrigglesworth, R.; Edge, S. J. *J. Org. Chem* **1993**, *58*, 5944 and references cited therein.

(2) For an example of epoxy acetates, see: Coxon, J. M.; Hartshorn, M. P.; Kirk, D. N. *Tetrahedron* **1964**, *20*, 2531; **1964**, *20*, 2547. In these cases, however, the yields of the rearranged products were very low and the regioselective cleavage of the oxirane ring was not observed.

(3) Pittman, C. U., Jr.; McManus, S. P.; Larsen, J. W. *Chem. Rev.* **1972**, *72*, 357.

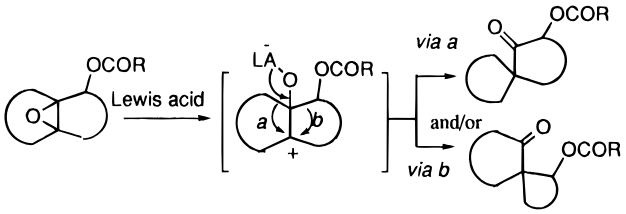
(4) Fujioka, H.; Kitagaki, S.; Imai, R.; Kondo, M.; Okamoto, S.; Yoshida, Y.; Akai, S.; Kita, Y. *Tetrahedron Lett.* **1995**, *36*, 3219.

(5) Devon, T. K.; Scott, A. I. *Handbook of Naturally Occurring Compounds*; Academic Press: New York, 1972; Vol. II. Marshall, J. A.; Brady, S. F.; Andersen, N. H. *Fortsch Chem. Org. Naturst.* **1974**, *31*, 283. Vandewalle, M.; De Clercq, P. *Tetrahedron* **1985**, *41*, 1767.

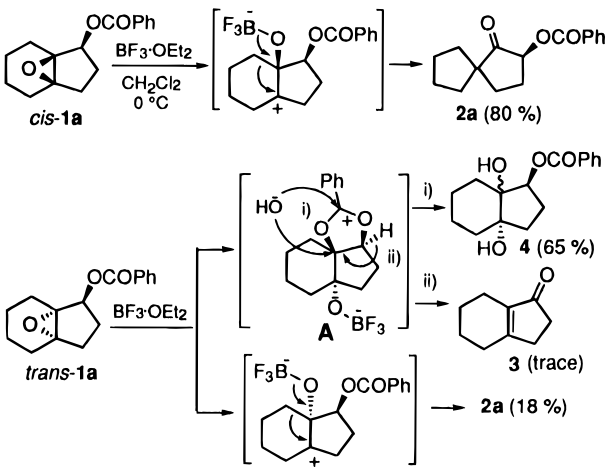
(6) Nakadaira, Y.; Hirota, Y.; Nakanishi, K. *J. Chem. Soc., Chem. Commun.* **1969**, 1467 and references cited therein.

S0022-3263(97)00035-2 CCC: $14.00 

**Scheme 2**



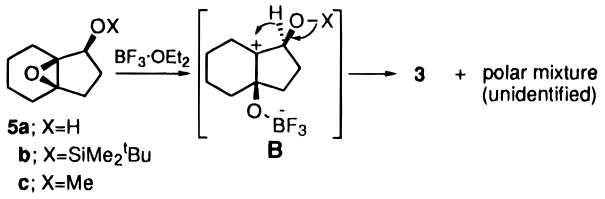

**Scheme 3**



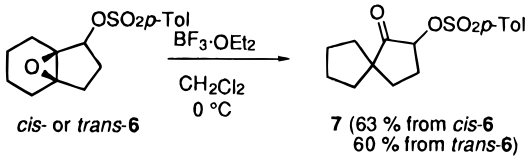

active spiro compounds.[8] Therefore, new methods for constructing chiral spiro compounds in optically active forms are strongly required. It seemed to us that a new method to stereoselectively obtain spiro compounds would be available, if the reaction shown in Scheme 1 successfully proceeded in bicyclic compounds (Scheme 2). Since α,*β*-epoxy alcohols can be easily prepared as optically active forms by the asymmetric reduction of enones followed by stereoselective epoxidation, this success should provide a new way to make optically active spiro compounds.

Initially, the inductive effect of an acyloxy group was examined using *cis*- and *trans*-epoxy benzoates in the bicyclo[4.3.0]alkane system (Scheme 3). The treatment of *cis*-epoxy benzoate (*cis*-**1a**) with $BF_3$·$OEt_2$ (1 equiv)

**Scheme 4**




**Scheme 5**




afforded the desired spiro compound, 2-(benzoyloxy)-1-oxospiro[4.4]nonane (**2a**), in 80% yield by regioselective cleavage of the epoxide at the *β*-position of the ester and successive skeletal rearrangement (corresponding to route a in Scheme 2).[9] On the other hand, *trans*-epoxy benzoate (*trans*-**1a**) gave the triol monobenzoates **4** as the major product and a trace of enone **3** accompanied with a small amount of the spiro compound **2a**. This was rationalized by the reaction through the dioxenium cation intermediate **A**, usually observed during the acid treatment of epoxy acylates. In this bicyclo system, the *cis*-epoxy alcohol **5a** and epoxy ethers **5b**,**c**, having the hydroxy moieties with the electron-donating ability, gave the enone **3** by cleavage of the epoxide at the α-position forming a cation intermediate **B** and successive hydride migration, followed by dehydration (Scheme 4). Therefore, it is suggested that selective *β*-cleavage of the epoxide of *cis*-**1a** results from the effect of the electron-withdrawing nature of the acyloxy group. The relative stereochemistries of the starting materials are very important for causing a rearrangement reaction, since neighboring group participation still played a significant role in the case of the *trans*-derivative, *trans*-**1a**. This was ascertained by the reaction of epoxy sulfonates **6**, which afforded the rearranged product **7** despite their stereochemistries. Thus even the *trans*-derivative afforded the corresponding spiro compound in good yield similar to the case of the *cis*-derivative because the sulfonyloxy group has a similar electron-withdrawing nature to the acyloxy group and less neighboring group participation (Scheme 5).

The reaction of several *cis*-epoxy acylates was next studied to examine the effect of the type of acyloxy group. Not only the benzoyloxy group but also other various acyloxy groups showed the same effect (Table 1). A variety of Lewis acids were also examined using *cis*-**1a**. As shown in Table 2, this rearrangement smoothly proceeded using $BF_3$·$OEt_2$ (entry 1). Lewis acids having the Cl ligand showed a tendency to give the Cl-adduct **8** rather than **2a** (entries 2, 4, and 6). On the other hand, $BF_3$·$OEt_2$ or $Al(OC_6F_5)_3$[10] having less nucleophilic ligand directly afforded **2a** in good yields (entries 1 and 3).

The present method was next applied to other bicyclic systems using $BF_3$·$OEt_2$ as the Lewis acid (Table 3). In the reactions of alkyl-substituted bicyclo[4.3.0]nonanes

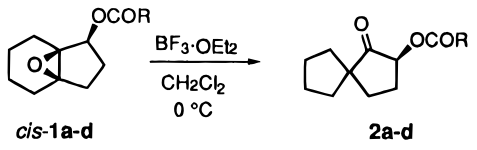
(7) For recent examples of spirocyclane systems, see: Tokunaga, Y.; Yagihashi, M.; Ihara, M.; Fukumoto, K. *J. Chem. Soc., Perkin Trans. 1*, **1997**, 189. Knolker, H.-J.; Jones, P. G.; Graf, R. *Synlett* **1996**, 1155. Sattelkau, T.; Hollmann, C.; Eilbracht, P. *Synlett* **1996**, 1221. Trost, B. M.; Chen, D. W. C. *J. Am. Chem. Soc.* **1996**, *118*, 12541. Hatsui, T.; Wang, J.-J.; Ikeda, S.; Takeshita, H. *Synlett* **1995**, 35. Patra, D.; Ghosh, S. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2635. Kuroda, C.; Hirono, Y. *Tetrahedron Lett.* **1994**, *35*, 6895. Provencal, D. P.; Leahy, J. W. *J. Org. Chem.* **1994**, *59*, 5496; Wu, Y.-J.; Zhu, Y.-Y.; Burnell, D. J. *J. Org. Chem.* **1994**, *59*, 104. Jenkins, T. J.; Burnell, D. J. *J. Org. Chem.* **1994**, *59*, 1485. Mandai, T.; Tsujiguchi, Y.; Tsuji, J.; Saito, S. *Tetrahedron Lett.* **1994**, *35*, 5701. Fuchs, K.; Paquette, L. A. *J. Org. Chem.* **1994**, *59*, 528. Sands, R. D. *J. Org. Chem.* **1994**, *59*, 468. Kessar, S. V.; Vohra, R.; Kaur, N. P.; Singh, K. N.; Singh, P. *J. Chem. Soc., Chem. Commun.* **1994**, 1327. Rao, A. V. R.; Singh, A. K.; Reddy, K. M.; Ravikumar, K. *J. Chem. Soc., Perkin Trans 1* **1993**, 3171 and references cited therein. For reviews, see: Krapcho, A. P. *Synthesis* **1974**, 383; **1976**, 425; **1978**, 77.

(8) For recent examples of the asymmetric synthesis of chiral spirocyclane systems, see: Takemoto, Y.; Kuraoka, S.; Ohra, T.; Yonetoku, Y.; Iwata, C. *Tetrahedron* **1997**, *53*, 603. Zhu, Y.-Y.; Burnell, D. J. *Tetrahedron: Asymmetry* **1996**, *7*, 3295. Huang, H.; Forsyth, C. J. *J. Org. Chem.* **1995**, *60*, 2773. Villar, J. M.; Delgado, A.; Llebaria, A.; Moreto, J. M. *Tetrahedron: Asymmetry* **1995**, *6*, 665. Chitkul, B.; Pinyopronpanich, Y.; Thebtaranonth, C.; Thebtaranonth, Y.; Taylor, W. C. *Tetrahedron Lett.* **1994**, *35*, 1099. Galvez, J. M. G.; Angers, P.; Canonne, P. *Tetrahedron Lett.* **1994**, *35*, 2849. Maezaki, N.; Fukuyama, H.; Yagi, S., Tanaka, T.; Iwata, C. *J. Chem. Soc., Chem. Commun.* **1994**, 1835. Knölker, H.-J.; Graf, R. *Tetrahedron Lett.* **1993**, *34*, 4765 and references cited therein. For review, see: Murai, A. *J. Synth. Org. Chem. Jpn.* **1981**, *39*, 893.

(9) $^1H-^1H$ COSY of the 1,2-diacetoxy derivatives obtained by $LiAlH_4$-reduction of the rearranged products followed by acetylation proved the presence of the 2-(acyloxy)-1-oxo moiety.

(10) Ishihara, K.; Hanaki, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 7074.

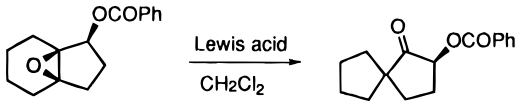
**Table 1. Study on the Effect of an Acyloxy Group**




*cis*-**1a-d** **2a-d**

| R | yield, % |
|---|---|
| **a** Ph | 80 |
| **b** Me | 71 |
| **c** *p*-$NO_2C_6H_4$ | 79 |
| **d** (−)-camphanoyl | 69 |

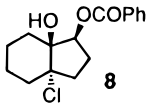
**Table 2. Study on the Effect of a Lewis Acid**




*cis*-**1a** **2a**

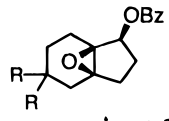
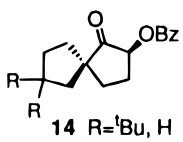
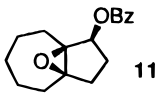
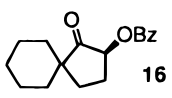
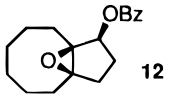
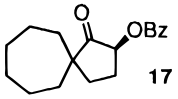
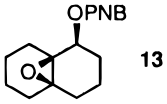
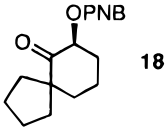
| Entry | Lewis acid (1 eq) | Condition | Yield, % |
|---|---|---|---|
| 1 | $BF_3·OEt_2$ | 0 °C, 3h | 80 |
| 2 | $EtAlCl_2$ | 0 °C, 4h | 45[a] |
| 3 | $Al(OC_6F_5)_3$ | reflux, 12h | 72 |
| 4 | $SnCl_4$ | 0 °C, 3h | 25[a] |
| 5 | $ZnBr_2$ | 0 °C - rt, 5h | 32 |
| 6 | $TiCl_4$ | -78 °C, 1h | 0[a] |

[a] Chlorohydrin **8** was obtained in yield as follows, respectively: entry 2, 35 %; entry 4, 39 %; entry 6, 64 %. **8** is a single isomer and its stereochemistry was deduced from mechanistic consideration.




**8**

**Table 3. Rearrangement Reaction of Bicyclic *cis*-Epoxy Acylates**

| Entry | Substrate | Product (Yield) |
|---|---|---|
| 1 |  **9** R=$^t$Bu, H[a] |  **14** R=$^t$Bu, H (58%) |
| 2 | **10** R=Me, Me | **15** R=Me, Me (95%) |
| 3 |  **11** |  **16** (99%) |
| 4 |  **12** |  **17** (55%) |
| 5[b] |  **13** |  **18** (41%) |

[a] A mixture of stereoisomers was used.
[b] Reaction was carried out in benzene under reflux.

**9**, **10**, bicyclo[5.3.0]decane **11**, and bicyclo[6.3.0]undecane **12** with an acyloxy group on a five-membered ring, the corresponding 2-(acyloxy)-1-oxospirocyclanes **14**−**17** were obtained by β-cleavage of the epoxide followed by successive contraction of the larger, non-acyloxy-substituted ring (corresponding to route a in Scheme 2), respectively (entries 1−4). During the reaction of bicyclo[4.4.0]decane **13**, a six-six membered compound, with an acyloxy-substitution on a six-membered ring, a similar reaction occurred to give the 2-(acyloxy)-1-oxo compound **18** (entry 5). This is due to low migratory aptitude of the acyloxy-

**Scheme 6**

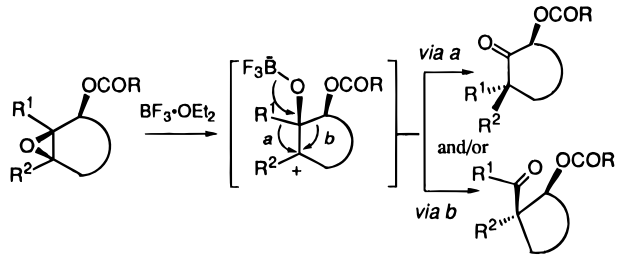
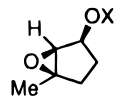
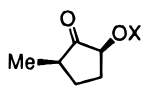
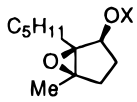
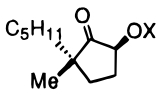
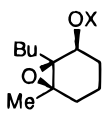
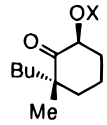
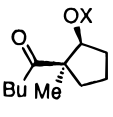



**Table 4. Rearrangement Reaction of Monocyclic *cis*-Epoxy Acylates**

| Entry | Substrate | Product (Yield) |
|---|---|---|
| 1 |  **19a**; X=Bz |  **22a**; X=Bz (81%) |
| 2 | **19b**; X=PNB | **22b**; X=PNB (79%) |
| 3 |  **20a**; X=Bz |  **23a**; X=Bz (61%) |
| 4 | **20b**; X=PNB | **23b**; X=PNB (73%) |
| 5 |  **21a**; X=Bz |  **24a**; X=Bz (37%)  **25a**; X=Bz (32%) |
| 6 | **21b**; X=PNB | **24b**; X=PNB (34%) **25b**; X=PNB (24%) |

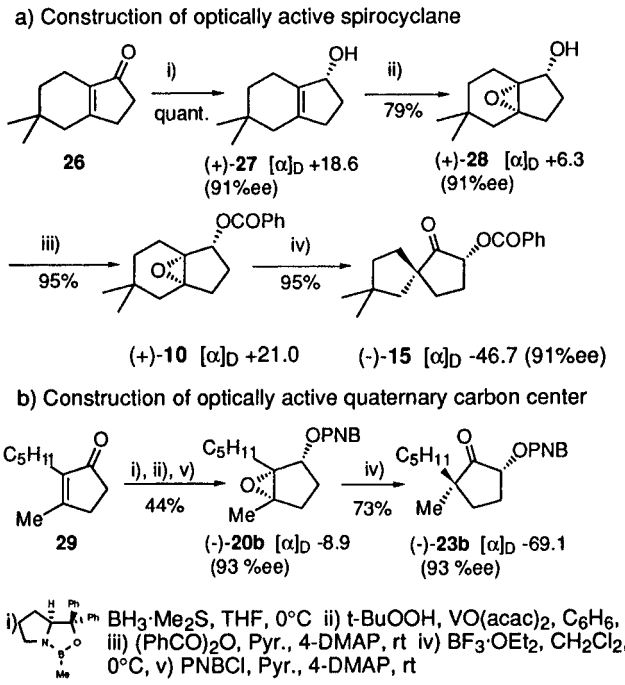
lated carbon because of the strong electron-withdrawing nature of the acyloxy function.

**Rearrangement Reaction in Monocyclic Systems: Synthesis of the Quaternary Carbon Center.** As mentioned in the preceding section, treatment of the *cis*-epoxy acylates in bicyclic systems with a Lewis acid did not cause neighboring group participation to afford spirocyclic compounds by stereoselective rearrangement. We then postulated that a stereoselective method to construct quaternary carbon centers could be developed if a similar reaction would occur in monocyclic systems (Scheme 6). Since chiral quaternary carbon centers are found in many biologically active natural products, construction of such structural subunits has been one of the challenging areas in synthetic organic chemistry, and many methodologies have been developed so far.[11]

The results of the rearrangement reactions of monocyclic *cis*-epoxy acylates are shown in Table 4. First the reaction of the epoxides on the cyclopentane ring systems was studied. Treatment of 2,3,3-trisubstituted epoxy acylates **19a,b** with $BF_3·OEt_2$ afforded the rearranged products formed through β-cleavage of the oxirane ring followed by successive hydride migration (corresponding to route a in Scheme 2) in good yields (entries 1 and 2). Tetrasubstituted epoxy acylates **20a,b** reacted in the same manner to yield α-acyloxy cyclopentanones **23a,b** having chiral quaternary carbon center at the α′-position

(11) For examples, see: Jung, M. E.; D'Amico, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 7379. Fuji, K. *Chem. Rev.* **1993**, *93*, 2037. d'Angelo, J.; Desmaële, D.; Dumas, F.; Guingant, A. *Tetrahedron: Asymmetry* **1992**, *3*, 459. Martin S. F. *Tetrahedron* **1980**, *36*, 419.

**Scheme 7**




(entries 3 and 4). In the cases of cyclopentane ring systems no ring-contracted product, or rearranged product through route b in Scheme 6, was obtained. This might be due to the unfavorable formation of a four-membered ring. On the other hand, in the case of the six membered ring **21**, ring contraction competed with migration of the alkyl chain to afford **24**, rearranged product through route a in Scheme 6, and **25**, rearranged product through route b in Scheme 6, respectively (entries 5 and 6).

**Construction of the Optically Active Spirocyclane System and Quaternary Carbon Center.** We demonstrated the applicability of the present method for the syntheses of optically active compounds as shown in Scheme 7. Thus, the asymmetric reduction of the enone **26** using Corey's method[12] afforded the (+)-allylic alcohol ((+)-**27**). Epoxidation of (+)-**27** with *t*-BuOOH/VO(acac)$_2$[13] gave *cis*-epoxy alcohol (+)-**28** as a single isomer. The ee values of (+)-**27** and (+)-**28** were determined as 91% for each product from the $^1$H NMR spectrum of the MTPA ester of (+)-**28**. The *cis*-epoxy alcohol ((+)-**28**) was converted to the benzoate (+)-**10**. The treatment of (+)-**10** with $BF_3$·$OEt_2$ gave an optically active spirocyclane (−)-**15**, whose optical purity was determined as 91% from its $^1$H NMR experiment using a chiral shift reagent [Eu(hfc)$_3$]. This result shows that the optical purity was completely retained during the rearrangement reaction. We next applied the method to the monocyclic system and succeeded in the formation of an optically active quaternary carbon center. Namely, the same procedure as described above converted the enone **29** to (−)-**23b** via the *cis*-epoxy acylate (−)-**20b**.[12] The ee values of (−)-**20b** and (−)-**23b** were determined as 93% for each product from the HPLC analysis using DAICEL Chiralcel OD for (−)-**20b** and an $^1$H NMR experiment using a chiral shift reagent [Eu(hfc)$_3$] for (−)-**23b**. In this case, complete retention of optical purity was also observed.

## Conclusion

A novel rearrangement reaction of cyclic α,β-epoxy acylates, stereoselectively prepared from the corresponding allylic alcohols, was developed using the electron-withdrawing nature of an acyloxy group. The present reaction proceeds stereoselectively and is applicable not only to the syntheses of a variety of spirocyclane systems or quaternary carbon centers on the rings but also to the syntheses of their optically active forms. Since many methodologies for constructing allylic alcohols in both enantiomeric forms have been established, this method promises the syntheses of many spiro compounds and compounds with a quaternary carbon center in both enantiomeric forms. Further application of this methodology to organic synthesis is currently under investigation.

## Experimental Section

All melting points are uncorrected. NMR spectra were measured on 270 MHz and 500 MHz spectrometers with $CDCl_3$ as a solvent and with $SiMe_4$ as an internal standard. Infrared (IR) absorption spectra were recorded as a KBr pellet. All solvents were dried and distilled according to standard procedure.

**Preparation of Epoxy Alcohol Derivatives.** *cis*-Epoxy acylates *cis*-**1**, **9**−**13**, and **19**−**21** were prepared from the corresponding α,β-unsaturated ketones, synthesized by the literature procedures[14], in a three-step sequence: (i) formation of allylic alcohol by reduction of the enone with DIBAH in $CH_2Cl_2$ at 0 °C, (ii) *cis*-epoxy alcohol formation by Sharpless epoxidation of the allylic alcohol with *t*-BuOOH/VO(acac)$_2$ in benzene according to the literature procedures[13], and (iii) acylation of epoxy alcohol with acid chloride (or acid anhydride) in pyridine (cf. Scheme 7). Silyl ether **5b** was prepared by silylation of **5a** with *t*-Bu$Me_2$SiCl and $Et_3N$ in $CH_2Cl_2$ at 0 °C. Methyl ether **5c** was prepared by methylation of **5a** with MeI and NaH in THF at 0 °C. *trans*-**1a** was prepared by epimerization of *cis*-epoxy alcohol **5a** by the Mitsunobu reaction using benzoic acid.[15] *cis*-Tosylate (*cis*-**6**) was prepared by tosylation of *cis*-epoxy alcohol **5a** using tosyl chloride in pyridine, and *trans*-tosylate (*trans*-**6**) was prepared by hydrolysis of *trans*-**1a** followed by tosylation.

***cis*-1,6-Epoxybicyclo[4.3.0]non-7-yl benzoate (*cis*-1a):** colorless oil; IR 2936, 1719, 1281 cm$^{-1}$; $^1$H NMR δ 1.20−2.20 (m, 12H), 5.34 (t, 1H, $J$ = 8.0 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.55 (t, 1H, $J$ = 7.5 Hz), 8.09 (d, 2H, $J$ = 7.5 Hz); $^{13}$C NMR δ 19.6, 19.9, 24.3, 25.2, 26.5, 29.7, 64.6, 65.6, 78.7, 128.2, 129.7, 130.1, 132.9, 166.7. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.58; H, 7.17.

***trans*-1,6-Epoxybicyclo[4.3.0]non-7-yl benzoate (*trans*-1a):** colorless oil; IR 2856, 1720, 1271 cm$^{-1}$; $^1$H NMR δ 1.25−2.20 (m, 12H), 5.44 (d, 1H, $J$ = 5.0 Hz), 7.46 (t, 2H, $J$ = 7.5 Hz), 7.58 (t, 1H, $J$ = 7.5 Hz), 8.01 (d, 2H, $J$ = 7.5 Hz); $^{13}$C NMR δ 20.0, 20.5, 22.2, 26.3, 28.0, 29.8, 65.9, 67.2, 76.8, 128.4, 129.5, 130.2, 133.0, 165.7. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.34; H, 7.16.

***cis*-1,6-Epoxybicyclo[4.3.0]non-7-yl acetate (1b):** colorless oil; IR 2928, 1740, 1242 cm$^{-1}$; $^1$H NMR δ 1.20−2.20 (m, 12H), 2.09 (s, 3H), 5.12 (t, 1H, $J$ = 8.0 Hz). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.27; H, 8.34.

***cis*-1,6-Epoxybicyclo[4.3.0]non-7-yl *p*-nitrobenzoate (1c):** white powder; mp 89−90 °C (hexane/ethyl acetate); IR 2938, 1725, 1273 cm$^{-1}$; $^1$H NMR δ 1.20−2.30 (m, 12H), 5.37 (t, 1H, $J$ = 8.5 Hz), 8.25 (ABq, 2H, $J$ = 8.0 Hz), 8.35 (ABq, 2H, $J$ =

(12) Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C-P. Singh, V. K. *J. Am. Chem. Soc.* **1987**, *109*, 7925. Absolute configurations of (+)-**27** and (−)-**20** were deduced by referring to the literature.

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

(14) Hiyama, T.; Shinoda, M.; Tsukanaka, M.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1010.

(15) Mitsunobu, O. *Synthesis* **1981**, 1.

8.0 Hz). Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.46; H, 5.65; N, 4.58.

***cis*-1,6-Epoxybicyclo[4.3.0]non-7-yl camphanoate (1d)** (1:1 diastereomeric mixture): white glassy oil; IR 2936, 1790, 1750, 1265 $cm^{-1}$; $^1H$ NMR $\delta$ 0.97, 0.98 (each s, total 3H), 1.07, 1.09 (each s, total 3H), 1.12 (s, 3H), 1.20−2.20 (m, 15H), 2.35−2.55 (m, 1H), 5.24 (dd, 1H, $J$ = 6.5, 13.0 Hz). Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 68.29; H, 7.89.

***cis*-1,6-Epoxybicyclo[4.3.0]nonan-7-ol (5a):** white powder; mp 103−104 °C (hexane/ethyl acetate); IR 3400, 2936 $cm^{-1}$; $^1H$ NMR $\delta$ 1.20−2.10 (m, 12H), 4.07 (t, 1H, $J$ = 8.5 Hz). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.03; H, 9.14.

***cis*-1,6-Epoxy-7-(*tert*-butyldimethylsiloxy)bicyclo[4.3.0]-nonane (5b):** colorless oil; IR 2936, 1472, 1256 $cm^{-1}$; $^1H$ NMR $\delta$ 0.05 (s, 3H), 0.07 (s, 3H), 0.89 (s, 9H), 1.15−1.45 (m, 6H), 1.50−1.65 (m, 3H), 1.80−2.00 (m, 3H), 4.07 (t, 1H, $J$ = 8.5 Hz). Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51; Si, 10.46. Found: C, 66.95; H, 10.48.

***cis*-1,6-Epoxy-7-methoxybicyclo[4.3.0]nonane (5c):** colorless oil; IR 2940, 1281 $cm^{-1}$; $^1H$ NMR $\delta$ 1.10−2.20 (m, 12H), 3.39 (s, 3H), 3.77 (t, 1H, $J$ = 8.5 Hz). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.50; H, 9.62.

***cis*-1,6-Epoxybicyclo[4.3.0]non-7-yl *p*-toluenesulfonate (*cis*-6):** colorless crystals; mp 70.5−72 °C (hexane/ethyl acetate); IR 2940, 1362, 1188, 1177 $cm^{-1}$; $^1H$ NMR $\delta$ 1.35−2.45 (m, 12H), 2.47 (s, 3H), 5.00 (dd, 1H, $J$ = 5.5, 9.0 Hz), 7.36 (d, 2H, $J$ = 8.0 Hz), 7.80 (d, 2H, $J$ = 8.0 Hz). Anal. Calcd for $C_{16}H_{20}SO_4$: C, 62.32; H, 6.54; S, 10.40. Found: C, 62.35; H, 6.53; S,10.33.

***trans*-1,6-Epoxybicyclo[4.3.0]non-7-yl *p*-toluenesulfonate (*trans*-6):** colorless oil; IR 2940, 1366, 1190, 1177 $cm^{-1}$; $^1H$ NMR $\delta$ 1.14−1.50 (m, 4H), 1.55−2.05 (m, 8H), 2.46 (s, 3H), 4.81 (br, 1H), 7.35 (d, 2H, $J$ = 8.0 Hz), 7.80 (d, 2H, $J$ = 8.0 Hz); $^{13}C$ NMR $\delta$ 19.5, 19.9, 21.4, 25.7, 27.8, 29.1, 53.3, 65.0, 67.1, 83.7, 127.6, 129.7, 133.6, 144.7; HRMS *m*/*z* Calcd for $C_{16}H_{20}SO_4$ ($M^+$): 308.1082. Found: 308.1063. Anal. Calcd for $C_{16}H_{20}SO_4$: C, 62.32; H, 6.54; S, 10.40. Found: C, 62.58; H, 6.69; S,10.10.

***cis*-1,6-Epoxy-3-*tert*-butylbicyclo[4.3.0]non-7-yl benzoate (9)** (1:1 diastereomeric mixture): colorless oil; IR 2957, 1719, 1273 $cm^{-1}$; $^1H$ NMR ($C_6D_6$) $\delta$ 0.72, 0.73 (each s, total 9H), 0.96−2.26 (m, 11H), 5.39, 5.41 (each t, total 1H, $J$ = 8.0, 8.5 Hz), 7.04 (t, 2H, $J$ = 7.5 Hz), 7.11 (t, 1H, $J$ = 7.5 Hz), 8.23 (m, 2H); HRMS *m*/*z* Calcd for $C_{20}H_{26}O_3$ ($M^+$): 314.1882. Found: 314.1881.

***cis*-1,6-Epoxy-3,3-dimethylbicyclo[4.3.0]non-7-yl benzoate (10):** colorless oil; IR 2953, 1721, 1273 $cm^{-1}$; $^1H$ NMR $\delta$ 0.84 (s, 3H), 0.92 (s, 3H), 1.10−2.18 (m, 10H), 5.34 (t, 1H, $J$ = 7.5 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.56 (t, 1H, $J$ = 7.5 Hz), 8.09 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR $\delta$ 21.4, 25.5, 25.8, 28.6, 30.6, 30.7, 31.7, 40.1, 64.6, 65.1, 78.3, 128.3, 129.7, 130.0, 133.0, 166.7; HRMS *m*/*z* Calcd for $C_{18}H_{22}O_3$ ($M^+$): 286.1569. Found: 286.1542. Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74. Found: C, 75.68; H, 7.83.

***cis*-1,7-Epoxybicyclo[5.3.0]decan-8-yl benzoate (11):** white powder; mp 85−86 °C (hexane/ethyl acetate); IR 2926, 1719, 1273 $cm^{-1}$; $^1H$ NMR $\delta$ 0.93−2.30 (m, 14H), 5.28 (t, 1H, $J$ = 8.0 Hz), 7.44 (t, 2H, $J$ = 7.0 Hz), 7.56 (t, 1H, $J$ = 7.0 Hz), 8.10 (d, 2H, $J$ = 7.0 Hz); $^{13}C$ NMR $\delta$ 24.9, 25.0, 25.1, 27.6, 30.1, 30.7, 31.4, 68.9, 69.9, 78.0, 128.3, 129.8, 130.1, 133.0, 166.6; HRMS *m*/*z* Calcd for $C_{17}H_{20}O_3$ ($M^+$): 272.1412. Found: 272.1420.

***cis*-1,8-Epoxybicyclo[6.3.0]undecan-9-yl benzoate (12):** white powder; mp 66−67 °C (hexane/ethyl acetate); IR 2953, 1719, 1275 $cm^{-1}$; $^1H$ NMR $\delta$ 1.10−2.40 (m, 16H), 5.48 (t, 1H, $J$ = 8.0 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.56 (t, 1H, $J$ = 7.5 Hz), 8.10 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR ($C_6D_6$) $\delta$ 24.7, 25.0, 25.2, 25.8, 26.1, 26.2, 26.9, 29.1, 66.9, 68.2, 75.1, 127.6, 128.0, 128.3, 130.1, 130.7, 133.0, 166.4. Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74. Found: C, 75.32; H, 7.77.

***cis*-1,6-Epoxybicyclo[4.4.0]decan-7-yl *p*-nitrobenzoate (13):** white powder; mp 107−108 °C (hexane/ethyl acetate); IR 2940, 1721, 1275 $cm^{-1}$; $^1H$ NMR $\delta$ 1.20−2.10 (m, 14H), 5.36 (dd, 1H, $J$ = 6.0, 8.0 Hz), 8.24−8.28 (m, 4H); $^{13}C$ NMR $\delta$ 19.1, 19.6, 20.4, 25.6, 26.8, 29.1, 31.2, 62.1, 64.3, 76.8, 123.5, 130.9, 135.7, 150.6, 164.6. Anal. Calcd for $C_{17}H_{19}NO_5$: C, 64.34; H, 6.03; N, 4.41. Found: C, 64.19; H, 6.02; N, 4.35.

***cis*-2,3-Epoxy-3-methylcyclopent-1-yl benzoate (19a):** colorless oil; IR 2959, 2932, 1721, 1275 $cm^{-1}$; $^1H$ NMR $\delta$ 1.48 (s, 3H), 1.60−1.80 (m, 2H), 1.95−2.18 (m, 2H), 3.53 (s, 1H), 5.35 (dd, 1H, $J$ = 7.0, 8.5 Hz), 7.43 (t, 2H, $J$ = 7.0 Hz), 7.55 (t, 1H, $J$ = 7.0 Hz), 8.08 (d, 2H, $J$ = 7.0 Hz); $^{13}C$ NMR $\delta$ 17.7, 24.9, 29.7, 62.4, 62.5, 75.9, 128.2, 129.6, 129.9, 132.9, 166.5. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.68; H, 6.58.

***cis*-2,3-Epoxy-3-methylcyclopent-1-yl *p*-nitrobenzoate (19b):** colorless needles; mp 136−137 °C (MeOH); IR 3115, 2986, 1721, 1275 $cm^{-1}$; $^1H$ NMR $\delta$ 1.51 (s, 3H), 1.55−1.80 (m, 2H), 2.05−2.18 (m, 2H), 3.55 (s, 1H), 5.39 (t, 1H, $J$ = 8.0 Hz), 8.25 (d, 2H, $J$ = 8.5 Hz), 8.29 (d, 2H, $J$ = 8.5 Hz). Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.30; H, 4.98; N, 5.34. Found: C, 59.36; H, 4.93; N, 5.35.

***cis*-2,3-Epoxy-3-methyl-2-pentylcyclopent-1-yl benzoate (20a):** colorless oil; IR 2959, 1719, 1275 $cm^{-1}$; $^1H$ NMR $\delta$ 0.85 (t, 3H, $J$ = 7.0 Hz), 1.21−1.30 (m, 4H), 1.39 (s, 3H,), 1.36−1.59 (m, 4H), 1.62−1.71 (m, 1H), 1.85−1.95 (m, 1H), 2.00−2.17 (m, 2H), 5.41 (t, 1H, $J$ = 8.0 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.55 (t, 1H, $J$ = 7.5 Hz), 8.09 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR $\delta$ 13.9, 15.9, 22.4, 24.6, 24.8, 27.5, 30.3, 32.0, 65.8, 69.4, 76.2, 128.3, 129.8, 130.1, 133.0, 166.5. Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.22; H, 8.42.

***cis*-2,3-Epoxy-3-methyl-2-pentylcyclopent-1-yl *p*-nitrobenzoate (20b):** colorless crystals; mp 72.5−73.5 °C (hexane/ethyl acetate); IR 2957, 2930, 1725, 1275 $cm^{-1}$; $^1H$ NMR $\delta$ 0.86 (t, 3H, $J$ = 7.0 Hz), 1.24−1.40 (m, 5H), 1.41 (s, 3H), 1.46−1.58 (m, 3H), 1.65−1.73 (m, 1H), 1.85−1.92 (m, 1H), 2.05−2.17 (m, 2H), 5.45 (t, 1H, $J$ = 8.0 Hz), 8.26 (d, 2H, $J$ = 8.5 Hz), 8.30 (d, 2H, $J$ = 8.5 Hz). Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.84; H, 6.95; N, 4.22. Found: C, 64.86; H, 6.86; N, 4.17.

***cis*-2-Butyl-2,3-epoxy-3-methylcyclohex-1-yl benzoate (21a):** colorless oil; IR 2936, 1717, 1451, 1271 $cm^{-1}$; $^1H$ NMR $\delta$ 0.86 (t, 3H, $J$ = 7.0 Hz), 1.37 (s, 3H), 1.25−1.55 (m, 6H), 1.57−1.80 (m, 4H), 1.85−2.00 (m, 2H), 5.46 (dd, 1H, $J$ = 6.0, 8.0 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.56 (t, 1H, $J$ = 7.5 Hz), 8.11 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR $\delta$ 13.8, 18.6, 20.6, 22.8, 26.1, 27.4, 29.8, 30.1, 63.9, 65.4, 71.8, 128.3, 129.7, 130.3, 132.9, 166.2. Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.19; H, 8.46.

***cis*-2-Butyl-2,3-epoxy-3-methylcyclohex-1-yl *p*-nitrobenzoate (21b):** colorless oil; IR 2959, 2936, 1723, 1273 $cm^{-1}$; $^1H$ NMR $\delta$ 0.87 (t, 3H, $J$ = 7.0 Hz), 1.25−1.50 (m, 6H), 1.38 (s, 3H), 1.60−1.81 (m, 4H), 1.85−2.00 (m, 2H), 5.49 (t, 1H, $J$ = 6.5 Hz), 8.28 (ABq, 2H, $J$ = 8.5 Hz), 8.29 (ABq, 2H, $J$ = 8.5 Hz). Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64,84; H, 6.95; N, 4.22. Found: C, 64.53; H, 6.81; N, 4.17.

**Lewis Acid Treatment of α,β-Epoxy Acylates (1, 9−12, 19−21), α,β-Epoxy Tosylates (*cis*- and *trans*-6), and 5a−c: General Procedure.** To a solution of epoxy acylates or sulfonates (0.1 mmol) in dry $CH_2Cl_2$ (1 mL) was added $BF_3{\cdot}OEt_2$ or other Lewis acid (0.1mmol) at 0 °C under $N_2$, and the reaction mixture was stirred for 5 min to 5 h. After having been diluted with $CH_2Cl_2$, saturated aqueous $NaHCO_3$ was added to the mixture. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with brine, dried over $MgSO_4$ or $Na_2SO_4$, and concentrated. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate) to give the pure product.

**2-(Benzoyloxy)-1-oxospiro[4.4]nonane (2a).** *cis*-**1a** (916 mg, 3.55 mmol) and $BF_3{\cdot}OEt_2$ (0.450 mL, 3.55 mmol) gave **2a** as a white powder (730 mg, 80%): mp 52−53 °C (hexane/ethyl acetate); IR 2955, 1750, 1721 $cm^{-1}$; $^1H$ NMR $\delta$ 1.51−2.09 (m, 11H), 2.45−2.55 (m, 1H), 5.39 (t, 1H, $J$ = 9.5 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.57 (t, 1H, $J$ = 7.5 Hz), 8.07 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR $\delta$ 25.5, 25.7, 26.5, 32.9, 37.5, 38.6, 54.2 (spiro carbon), 75.9, 128.3, 129.5, 129.8, 133.2, 165.7, 217.0; HRMS *m*/*z* Calcd for $C_{16}H_{18}O_3$ ($M^+$): 258.1256. Found: 258.1244. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 74.12; H, 7.07.

**Triol monobenzoate (4).** *trans*-**1a** (50 mg, 0.19 mmol) and $BF_3{\cdot}OEt_2$ (25 μL, 0.2 mmol) gave **2a** (9.0 mg, 18%) and **4** as a glassy oil (34 mg, 65%). **4**; triol monobenzoate (more polar

product on TLC (hexane/ethyl acetate = 5/1): $R_f$ = 0.1); IR 3500, 2863, 1710 cm$^{-1}$; $^1$H NMR $\delta$ 1.50−2.60 (m, 12H), 5.44 (dd, 1H, $J$ = 7.0, 10.0 Hz), 7.45 (t, 2H, $J$ = 7.5 Hz), 7.57 (t, 1H, $J$ = 7.5 Hz), 8.03 (d, 2H, $J$ = 7.5 Hz). **4**; triol monobenzoate (less polar product on TLC (hexane/ethyl acetate = 5/1): $R_f$ = 0.2); IR 3400, 2865, 1700 cm$^{-1}$; $^1$H NMR $\delta$ 1.50−2.30 (m, 11H), 2.90−3.10 (m, 1H), 4.60 (t, 1H, $J$ = 8.5 Hz), 7.46 (t, 2H, $J$ = 7.5 Hz), 7.60 (t, 1H, $J$ = 7.5 Hz), 8.02 (d, 2H, $J$ = 7.5 Hz).

**2-Acetoxy-1-oxospiro[4.4]nonane (2b).** *cis*-**1b** (30 mg, 0.153 mmol) and $BF_3$·$OEt_2$ (19 $\mu$L, 0.153 mmol) gave **2b** as a colorless oil (21.3 mg, 71%): IR 2955, 1742 cm$^{-1}$; $^1$H NMR $\delta$ 1.50−2.00 (m, 11H), 2.14 (s, 3H), 2.36−2.55 (m, 1H), 5.15 (t, 1H, $J$ = 10.5 Hz); $^{13}$C NMR $\delta$ 20.7, 25.5, 25.7, 26.4, 32.9, 37.5, 38.6, 54.2 (spiro carbon), 75.5, 170.2, 217.2. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.33; H, 8.21. Found: C, 67.34; H, 8.19.

**2-[(*p*-Nitrobenzoyl)oxy]-1-oxospiro[4.4]nonane (2c).** *cis*-**1c** (1.0 g, 3.3 mmol) and $BF_3$·$OEt_2$ (0.41 mL, 3.3 mmol) gave **2c** as colorless crystals (793 mg, 79%): mp 108−109 °C ($CH_2$-$Cl_2$/hexane); IR 2955, 2869, 1750, 1730 cm$^{-1}$; $^1$H NMR $\delta$ 1.20−2.20 (m, 11H), 2.40−2.60 (m, 1H), 5.43 (dd, 1H, $J$ = 8.5, 10.0 Hz), 8.24 (d, 2H, $J$ = 8.5 Hz), 8.30 (d, 2H, $J$ = 8.5 Hz); $^{13}$C NMR $\delta$ 25.8, 26.0, 26.7, 33.2, 37.9, 39.0, 54.5 (spiro carbon), 77.0, 123.8, 131.3, 135.2, 150.9, 164.2, 216.6. Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.31; H, 5.63, N, 4.62.

**2-(Camphanoyloxy)-1-oxospiro[4.4]nonane (2d).** *cis*-**1d** (60 mg, 0.180 mmol) and $BF_3$·$OEt_2$ (22 $\mu$L, 0.180 mmol) gave **2d** as a white solid (41.6 mg, 69%): mp 75.5−77 °C (hexane/ethyl acetate); IR 2971, 1790, 1748 cm$^{-1}$; $^1$H NMR $\delta$ 1.04 (s, 3H), 1.08 (s, 3H), 1.12 (s, 3H), 1.20−2.60 (m, 16H), 5.35 (dd, 1H, $J$ = 8.0, 10.0 Hz). Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 67.90; H, 7.86.

**2-*p*-Toluenesulfonyl-1-oxospiro[4.4]nonane (7).** *cis*-**6** (38.8 mg, 0.126 mmol) and $BF_3$·$OEt_2$ (20 $\mu$L, 0.126 mmol) gave **7** as a pale yellow powder (24.5 mg, 63%): mp 83−84 °C (hexane/ethyl acetate); IR 2870, 1754, 1368, 1176 cm$^{-1}$; $^1$H NMR $\delta$ 1.20−2.10 (m, 11H), 2.30−2.50 (m, 1H), 2.45 (s, 3H), 4.77 (dd, 1H, $J$ = 8.5, 9.5 Hz), 7.34 (d, 2H, $J$ = 8.5 Hz), 7.85 (d, 2H, $J$ = 8.5 Hz); $^{13}$C NMR $\delta$ 21.7, 25.5, 25.7, 27.5, 32.6, 37.1, 38.6, 53.9 (spiro carbon), 80.1, 128.0, 129.8, 133.5, 144.9, 214.3; HRMS *m*/*z* Calcd for $C_{16}H_{20}SO_4$ ($M^+$): 308.1083. Found: 308.1077.

**2-*p*-Toluenesulfonyl-1-oxospiro[4.4]nonane (7).** *trans*-**6** (412 mg, 1.34 mmol) and $BF_3$·$OEt_2$ (0.165 mL, 1.34 mmol) gave **7** (247 mg, 60%).

**(1α,6α,7*β*)-1-Chloro-6-hydroxybicyclo[4.3.0]non-7-yl benzoate (8):** colorless oil: IR 3400, 1723, 1279 cm$^{-1}$; $^1$H NMR $\delta$ 1.45−2.20 (m, 10H), 2.35−2.47 (m, 1H), 2.57−2.70 (m, 1H), 5.59 (dd, 1H, $J$ = 5.5, 9.0 Hz), 7.45 (t, 2H, $J$ = 7.5 Hz), 7.57 (t, 1H, $J$ = 7.5 Hz), 8.02 (d, 2H, $J$ = 7.5 Hz); HRMS *m*/*z* Calcd for $C_9H_{13}OCl$ ($M^+$ − PhCOOH): 172.0655. Found: 172.0673.

**2-(Benzoyloxy)-7-*tert*-butyl-1-oxospiro[4.4]nonane (14).** **9** (49.7 mg, 0.158 mmol) and $BF_3$·$OEt_2$ (20 $\mu$L, 0.158 mmol) gave **14** as a colorless oil (29.0 mg, 58%): IR 2957, 2867, 1752, 1725 cm$^{-1}$; $^1$H NMR $\delta$ 0.87, 0.89 (each s, total 9H), 1.34−2.15 (m, 10H), 2.40−2.50 (m, 1H), 5.35, 5.38 (m, dd, total 1H, $J$ = 8.5, 11.0 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.56 (t, 1H, $J$ = 7.5 Hz), 8.07 (d, 2H, $J$ = 7.5 Hz). Anal. Calcd for $C_{20}H_{26}O_3$: C, 76.40; H, 8.33. Found: C, 76.40; H, 8.28.

**2-(Benzoyloxy)-7,7-dimethyl-1-oxospiro[4.4]nonane (15).** **10** (58 mg, 0.2 mmol) and $BF_3$·$OEt_2$ (25 $\mu$L, 0.2 mmol) gave **15** as a colorless oil (55.0 mg, 95%): IR 2953, 1752, 1723 cm$^{-1}$; $^1$H NMR $\delta$ 1.09 (s, 3H), 1.10 (s, 3H), 1.42−1.98 (m, 7H), 2.01−2.20 (m, 2H), 2.44−2.50 (m, 1H), 5.35 (t, 1H, $J$ = 9.0 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.57 (t, 1H, $J$ = 7.5 Hz), 8.05 (d, 2H, $J$ = 7.5 Hz); $^{13}$C NMR $\delta$ 26.4, 29.2, 29.5, 34.8, 37.5, 40.5, 41.5, 52.7, 54.7 (spiro carbon), 75.5, 128.4, 129.6, 129.9, 133.2, 165.9, 216.9. Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74. Found: C, 75.19; H, 7.85.

**2-(Benzoyloxy)-1-oxospiro[4.5]decane (16).** **11** (47.2 mg, 0.173 mmol) and $BF_3$·$OEt_2$ (20 $\mu$L, 0.173 mmol) gave **16** as a white powder (46.7 mg, 99%): mp 62−63 °C (hexane/ethyl acetate); IR 2930, 2857, 1752, 1721 cm$^{-1}$; $^1$H NMR $\delta$ 1.33−2.60 (m, 14H), 5.43 (dd, 1H, $J$ = 8.0, 11.0 Hz), 7.39−7.57 (m, 3H), 8.04−8.09 (m, 2H); $^{13}$C NMR $\delta$ 22.6, 22.8, 26.4, 26.7, 30.1, 32.5, 35.5, 48.2 (spiro carbon), 77.0, 129.3, 130.5, 130.8, 134.1, 166.7, 216.7; HRMS *m*/*z* Calcd for $C_{17}H_{20}O_3$ ($M^+$): 272.1412. Found: 272.1409.

**2-(Benzoyloxy)-1-oxospiro[4.6]undecane (17).** **12** (122.3 mg, 0.427 mmol) and $BF_3$·$OEt_2$ (57 $\mu$L, 0.427 mmol) gave **17** as a colorless oil (67.1 mg, 55%): IR 2921, 2855, 1752, 1725 cm$^{-1}$; $^1$H NMR $\delta$ 1.25−2.18 (m, 15H), 2.35−2.55 (m, 1H), 5.43 (dd, 1H, $J$ = 8.5, 11.0 Hz), 7.42 (t, 2H, $J$ = 7.5 Hz), 7.55 (t, 1H, $J$ = 7.5 Hz), 8.06 (d, 2H, $J$ = 7.5 Hz); $^{13}$C NMR $\delta$ 23.3, 23.4, 25.6, 29.7, 31.8, 35.6, 37.2, 49.6 (spiro carbon), 75.6, 128.3, 129.5, 129.9, 133.2, 165.8, 216.4; HRMS *m*/*z* Calcd for $C_{18}H_{22}O_3$ ($M^+$): 286.1569. Found: 286.1542.

**3-Methyl-2-oxocyclopent-1-yl Benzoate (22a). 19a** (183 mg, 0.887 mmol) and $BF_3$·$OEt_2$ (0.109 mL, 0.887 mmol) gave **22a** as a colorless oil (149 mg, 81%): IR 2936, 2876, 1757, 1725 cm$^{-1}$; $^1$H NMR $\delta$ 1.22 (d, 3H, $J$ = 7.5 Hz), 1.70−1.90 (m, 1H), 1.95−2.14 (m, 1H), 2.17−2.32 (m, 1H), 2.37−2.52 (m, 2H), 5.39 (dt, 1H, $J$ = 1.5, 8.5 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.57 (t, 1H, $J$ = 7.5 Hz), 8.39 (d, 2H, $J$ = 7.5 Hz); $^{13}$C NMR $\delta$ 15.7, 26.1, 26.4, 39.6, 76.5, 128.3, 129.8, 130.1, 133.2, 165.7, 214.3. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.46; H, 6.44.

**3-Methyl-2-oxocyclopent-1-yl *p*-Nitrobenzoate (22b). 19b** (448 mg, 1.69 mmol) and $BF_3$·$OEt_2$ (0.214 mL, 1.69 mmol) gave **22b** as colorless needles (353 mg, 79%): m.p. 109−110 °C (MeOH); IR 2970, 2878, 1757, 1728 cm$^{-1}$; $^1$H NMR $\delta$ 1.23 (d, 3H, $J$ = 7.5 Hz), 1.77−1.90 (m, 1H), 2.03−2.60 (m, 4H), 5.45 (dt, 1H, $J$ = 1.5, 9.0 Hz), 8.23 (d, 2H, $J$ = 8.5 Hz), 8.29 (d, 2H, $J$ = 8.5 Hz). Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.30; H, 4.98; N, 5.34. Found: C, 59.10; H, 4.91; N, 5.32.

**3-Methyl-2-oxo-3-pentylcyclopent-1-yl Benzoate (23a). 20a** (742 mg, 2.57 mmol) and $BF_3$·$OEt_2$ (0.326 mL, 2.57 mmol) gave **23a** as a colorless oil (455 mg, 61%): IR 2930, 1755, 1725 cm$^{-1}$; $^1$H NMR $\delta$ 0.88 (t, 3H, $J$ = 7.0 Hz), 1.14 (s, 3H), 1.19−1.52 (m, 8H), 1.80−2.02 (m, 3H), 2.42−2.52 (m, 1H), 5.36 (t, 1H, $J$ = 8.0 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.57 (t, 1H, $J$ = 7.5 Hz), 8.08 (t, 2H, $J$ = 7.5 Hz); $^{13}$C NMR $\delta$ 14.3, 22.8, 23.6, 24.3, 25.7, 30.5, 32.5, 38.5, 46.8 (quaternary carbon), 76.9, 128.7, 129.8, 130.2, 133.6, 166.1, 216.5. Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.80; H, 8.39.

**3-Methyl-2-oxo-3-pentylcyclopent-1-yl *p*-Nitrobenzoate (23b). 20b** (22.3 mg, 0.064 mmol) and $BF_3$·$OEt_2$ (8 $\mu$L, 0.064 mmol) gave **23b** as colorless crystals (16.2 mg, 73%): mp 59.5−61 °C (hexane); IR 2960, 2930, 1755, 1730 cm$^{-1}$; $^1$H NMR $\delta$ 0.89 (t, 3H, $J$ = 6.5 Hz), 1.15 (s, 3H), 1.12−1.58 (m, 8H), 1.85−2.10 (m, 3H), 2.45−2.55 (m, 1H), 5.40 (t, 1H, $J$ = 10.0 Hz), 8.24 (d, 2H, $J$ = 8.5 Hz), 8.29 (d, 2H, $J$ = 8.5 Hz); $^{13}$C NMR $\delta$ 14.0, 22.5, 23.3, 24.0, 25.3, 30.3, 32.2, 38.2, 46.6 (quaternary carbon), 77.4, 123.6, 131.1, 134.9, 150.8, 164.0, 215.6. Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.79; H, 6.90; N, 4.17.

**3-Butyl-3-methyl-2-oxocyclohex-1-yl Benzoate (24a)** and **2-Methyl-2-(1-oxopentyl)cyclopent-1-yl Benzoate (25a). 21a** (42.7 mg, 0.148 mmol) and $BF_3$·$OEt_2$ (18 $\mu$L, 0.148 mmol) gave **24a** (15.8 mg, 37%) and **25a** (13.5 mg, 32%). **24a:** colorless oil; IR 2936, 1732, 1721 cm$^{-1}$; $^1$H NMR $\delta$ 0.94 (t, 3H, $J$ = 7.0 Hz), 1.08 (s, 3H), 1.10−1.65 (m, 6H), 1.75−2.15 (m, 5H), 2.32−2.44 (m, 1H), 5.64 (dd, 1H, $J$ = 6.0, 13.0 Hz), 7.43 (t, 2H, $J$ = 7.5 Hz), 7.55 (t, 1H, $J$ = 7.5 Hz), 8.09 (d, 2H, $J$ = 7.5 Hz); $^{13}$C NMR $\delta$ 13.9, 19.4, 22.1, 23.3, 25.7, 33.3, 37.0, 40.1, 49.6 (quaternary carbon), 74.9, 128.3, 129.8, 133.0, 165.7, 208.3. Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.93; H, 8.32. **25a:** colorless oil; IR 2959, 2874, 1721 cm$^{-1}$; $^1$H NMR $\delta$ 0.90 (t, 3H, $J$ = 7.5 Hz), 1.30 (s, 3H), 1.25−1.35 (m, 2H), 1.50−1.87 (m, 6H), 2.15−2.20 (m, 2H), 2.55 (t, 2H, $J$ = 7.5 Hz), 5.64 (t, 1H, $J$ = 6.0 Hz), 7.44 (t, 2H, $J$ = 7.5 Hz), 7.57 (t, 1H, $J$ = 7.5 Hz), 8.03 (d, 2H, $J$ = 7.5 Hz). Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.02; H, 8.41.

**3-Butyl-3-methyl-2-oxocyclohex-1-yl *p*-Nitrobenzoate (24b) and 2-Methyl-2-(1-oxopentyl)cyclopent-1-yl *p*-Nitrobenzoate (25b). 21b** (50 mg, 0.15 mmol) and $BF_3$·$OEt_2$ (19 $\mu$L, 0.15 mmol) gave **24b** (17 mg, 34%) and **25b** (12 mg, 24%). **24b:** colorless oil; IR 2938, 1736, 1721 cm$^{-1}$; $^1$H NMR $\delta$ 0.95 (t, 3H, $J$ = 7.0 Hz), 1.08 (s, 3H), 1.10−1.65 (m, 6H,), 1.80−2.15 (m, 5H), 2.35−2.50 (m, 1H), 5.65 (dd, 1H, $J$ = 6.5, 12.5 Hz), 8.25 (d, 2H, $J$ = 9.0 Hz), 8.28 (d, 2H, $J$ = 9.0 Hz). Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.84; H, 6.95; N, 4.22. Found: C,

64.97; H, 6.81; N, 4.19. **25b:** colorless oil; IR 2955, 1727, 1707 $cm^{-1}$; $^1H$ NMR $\delta$ 0.91 (t, 3H, $J$ = 7.5 Hz), 1.24−1.40 (m, 2H), 1.31 (s, 3H), 1.52−1.90 (m, 6H), 2.11−2.30 (m, 2H), 2.54 (t, 2H, $J$ = 7.0 Hz), 5.70 (t, 1H, $J$ = 6.0 Hz), 8.18 (d, 2H, $J$ = 8.5 Hz), 8.28 (d, 2H, $J$ = 8.5 Hz); $^{13}C$ NMR $\delta$ 13.9, 18.1, 21.0, 22.4, 26.1, 31.0, 35.1, 37.2, 58.3 (quaternary carbon), 79.6, 123.6, 130.6, 135.7, 164.0, 212.4. Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.85; H, 6.87; N, 4.32.

**7-(*p*-Nitrobenzoyloxy)-6-oxospiro[4.5]decane (18).** To a solution of **13** (51.3 mg, 0.162 mmol) in dry benzene (1.7 mL) was added $BF_3$·$OEt_2$ (20 μL, 0.162 mmol) at rt, and the reaction mixture was refluxed for 3 h. After having been diluted with ethyl acetate, saturated aqueous $NaHCO_3$ was added to the mixture. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate) to gave **18** as colorless crystals (21.0mg, 41%): mp 103−104 °C (MeOH); IR 2869, 1736, 1721 $cm^{-1}$; $^1H$ NMR $\delta$ 1.14−2.00 (m, 12H), 2.38−2.55 (m, 2H), 5.63 (dd, 1H, $J$ = 5.5, 6.5 Hz), 8.25 (d, 2H, $J$ = 6.5 Hz), 8.29 (d, 2H, $J$ = 6.5 Hz); $^{13}C$ NMR $\delta$ 20.7, 24.5, 25.4, 32.6, 33.6, 35.6, 39.3, 57.0 (spiro carbon), 76.1, 123.3, 130.8, 135.2, 150.4, 163.7, 206.1. Anal. Calcd for $C_{17}H_{19}NO_5$: C, 64.34; H, 6.03; N, 4.41. Found: C, 64.29; H, 6.06; N, 4.41.

**(+)-(7*R*)-3,3-Dimethylbicyclo[4.3.0]non-1,6-en-7-ol (27).** To a solution of (*S*)-tetrahydro-1-methyl-3,3-diphenyl-1*H*,3*H*-pyrrolo[1,2-*c*][1.3.2]oxazaborole (1.18 mL) in dry THF (3 mL) was added $BH_3$·$Me_2S$ (2.0 M in THF, 0.85 mL, 1.7 mmol) at 0 °C under $N_2$, and the reaction mixture was stirred for 10 min. Then 3,3-dimethylbicyclo[4.3.0]non-1,6-en-7-one (**26**) (280 mg, 1.7 mmol), prepared from 4,4-dimethylcyclohexanone by a known method, in dry THF (10 mL) was added dropwise to the reaction mixture over 20 min. After being stirred for 30 min at rt, MeOH was added to the mixture and the resulting solution was stirred for 30 min. Then reaction mixture was evaporated, and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 4:1) to give the pure allylic alcohol (+)-**27** as a colorless oil (284 mg, quant): $[\alpha]_D$ +18.6 (*c* 0.39, $CHCl_3$); IR 3367, 2953 $cm^{-1}$; $^1H$ NMR $\delta$ 0.89 (s, 3H), 0.94 (s, 3H), 1.35−2.40 (m, 11H), 4.64 (br, 1H).

**(+)-(1*R*,6*R*,7*R*)-1,6-Epoxy-3,3-dimethylbicyclo[4.3.0]-nonan-7-ol (28).** To a solution of (+)-**27** (240 mg, 1.44 mmol) in benzene (4 mL) was added $VO(acac)_2$ (38 mg, 0.14 mmol) at rt under $N_2$, and *t*-BuOOH (70%, 0.60 mL, 4.39 mmol), dried over $MgSO_4$ in benzene (3 mL), was added to the reaction mixture. After being stirred for 20 min, saturated aqueous $Na_2SO_3$ was added to the mixture, and then the resulting solution was stirred for 30 min. The crude product was extracted with ethyl acetate. Orgnic layer was washed with brine and dried over $Na_2SO_4$. Purification of the concentrated crude material by column chromatography on silica gel (hexane/ethyl acetate = 4:1) to give (+)-**28** as colorless crystals (208 mg, 79%): mp 129−130 °C (hexane/ethyl acetate); $[\alpha]_D$ +6.3 (*c* 0.38, $CHCl_3$); IR 3250, 2951 $cm^{-1}$; $^1H$ NMR $\delta$ 0.80 (s, 3H), 0.90 (s, 3H), 1.11−2.17 (m, 11H), 4.07 (t, 1H, $J$ = 7.5 Hz); $^{13}C$ NMR $\delta$ 20.8, 25.8, 28.6, 29.5, 30.7, 30.8, 31.8, 40.3, 66.3, 66.9, 76.5. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.26; H, 9.85.

**(+)-(1*R*,6*R*,7*R*)-1,6-Epoxy-3,3-dimethylbicyclo[4.3.0]non-7-yl benzoate ((+)-10):** $[\alpha]_D$ +21.0 (*c* 0.70, $CHCl_3$).

**(−)-(2*R*,5*R*)-2-(Benzoyloxy)-7,7-dimethyl-1-oxospiro-[4.4]nonane ((−)-15):** $[\alpha]_D$ −46.7 (*c* 0.38, $CHCl_3$).

**(−)-(1*R*,2*R*,3*S*)-2,3-Epoxy-3-methyl-2-pentylcyclopent-1-yl *p*-Nitrobenzoate ((−)-20b).** The same procedure used for bicyclic enone **26** was employed. From **29** (31.1 mg, 0.187 mmol) there was obtained (−)-**20b** (28.4 mg, 71%): $[\alpha]_D$ −8.9 (*c* 0.55, $CHCl_3$). HPLC analysis of (±)-**20b** and (−)-**20b**; Daicel chiral cel OD; eluent, hexane/$^i$PrOH = 95/5; flow rate, 0.5 mL/min; retention time ($t_R$), 16.31 and 26.19 min for (±)-**20b** and 16.31 min for (−)-**20b**.

**(−)-(2*R*,5*R*)-5-Methyl-1-oxo-5-pentylcyclopent-2-yl *p*-nitrobenzoate ((−)-23b):** $[\alpha]_D$ −69.12 (*c* 0.38, $CHCl_3$).

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