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HYPERVALENT IODINE(III) REAGENT-PROMOTED REARRANGEMENT AND SUBSEQUENT OXIDATIVE RING CLEAVAGE OF CYCLIC 2,3-EPOXY-1-ALCOHOL DERIVATIVES†

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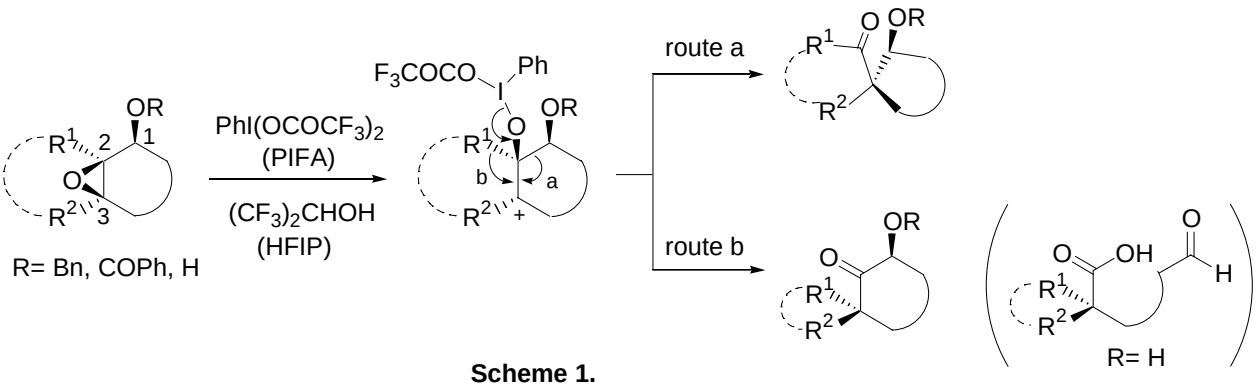
Abstract – The rearrangements of 2,3-epoxy alcohol derivatives were achieved using the hypervalent iodine(III) reagent, phenyliodine(III) bis(trifluoroacetate) (PIFA). In the case of 2,3-epoxy alcohols subsequent oxidative ring cleavage occurred to give ω-formylalkanoic acids.

INTRODUCTION

The rearrangements of epoxides and their derivatives are valuable tools for constructing carbonyl compounds and have been widely studied.[1] We have already reported the Lewis acid promoted regio- and stereoselective rearrangement of 2,3-epoxy alcohol derivatives.[2] On the other hand, hypervalent iodine(III) reagents have received much attention due to their low toxicity, ready availability, easy handling and reactivity similar to those of heavy metal reagents.[3] Furthermore, they have an interesting double reactivity: oxidation activity and Lewis acidity. In connection with our continuous studies on the chemistry of hypervalent iodine(III) reagents, we examined the reaction of 2,3-epoxy alcohol derivatives with hypervalent iodine(III) reagents in the presence of *O*-nucleophiles and quite recently found domino-type reaction.[4] However, to the best of our knowledge, there are no reports on the reaction of 2,3-epoxy alcohol derivatives with only hypervalent iodine(III) reagents.[5] In this paper, we report the rearrangements (routes a and b) and the tandem rearrangement and subsequent oxidative ring cleavage reaction (for R = H in route b) of 2,3-epoxy alcohol derivatives using the hypervalent iodine(III) reagent, phenyliodine(III) bis(trifluoroacetate) (PIFA) (Scheme 1).

†*This paper is dedicated to the memory of the late Professor Kenji Koga.*

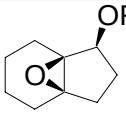
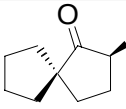
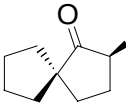
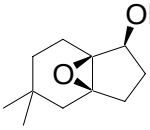
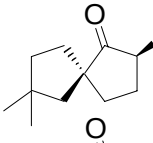
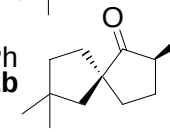
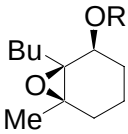
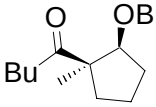
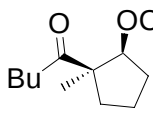
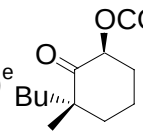


Scheme 1.

RESULTS AND DISCUSSION

We initially examined the reactivity of 2,3-epoxy alcohol derivatives having protecting groups with PIFA in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)[6] which is used as a low nucleophilic alcoholic solvent. As shown in Table 1, when the *cis*-2,3-epoxy alcohols were protected with the benzyl or benzoyl group, every reaction proceeded *via* the C3 carbocation to afford the rearranged products, α-hydroxy ketone and β-hydroxy ketone derivatives. The spectral data of the compounds ((±)-**4b,** (±)-**5b,** (±)-**6b,** (±)-**7**) were

Table 1. Reaction of 2, 3-epoxy alcohol derivatives having benzyl and benzoyl group with PIFA[a]

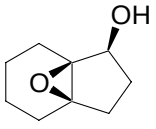
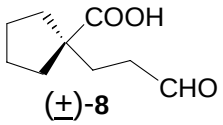
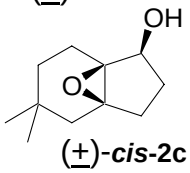
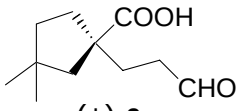
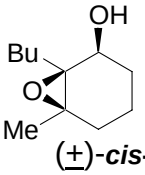
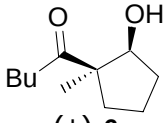
Entry	Substrate	Product	Yield (%)[b,c]
1	 R=Bn (±)-***cis*-1a**	 (±)-**4a**	53 (27)[d]
2	R=COPh (±)-***cis*-1b**	 (±)-**4b**	92 (80)[e]
3	 R=Bn (±)-***cis*-2a**	 (±)-**5a**	100 (71)
4	R=COPh (±)-***cis*-2b**	 (±)-**5b**	73 (95)[e]
5	 R=Bn (±)-***cis*-3a**	 (±)-**6a**	86 (81)[f]
6	R=COPh (±)-***cis*-3b**	 (±)-**6b**	17 (32)[e]  22 (37)[e] (±)-**7**

[a]Reactions were carried out with Substrate (1 equiv.) and PIFA (1 equiv.) in HFIP. [b]Isolated yields. [c]Yields in parentheses are the results of the reactions using $BF_3 \cdot Et_2O$ in CH_2Cl_2 instead of PIFA in THF. [d]Unidentified polar compound was also obtained. [e]Previous results reported by us.[2a] [f]Previous results reported by us.[2e]

identical with those already reported by us.[2a] Structures of (±)-**4a,** (±)-**5a**, and (±)-**6b**, were deduced from their spectral data and mechanistic considerations. This tendency for the compounds with benzoyloxy group (Entries 2, 4, 6) was similar to that observed in the Lewis acid–promoted rearrangement which has already been reported by us.[2] As we already concluded in our previous reports, we assume that the reason for the reactions of the epoxy benzoyl ester *via* the C3 carbocation intermediates is due to the destabilization of the C2 carbocation by the electron-withdrawing nature of the benzoyl group. In the cases of benzyl ethers, the yields by PIFA are higher than those by $BF_3 \cdot Et_2O$ (Entries 1, 3, 5). The fact means that PIFA rather acted like a Lewis acid, coordinated to the two oxygens from the oxirane ring and the benzyl ether, and accelerated the formation of the C3 carbocation (*vide infra*). Therefore, both the benzyl and benzoyl groups afforded the same tendency. Thus these results indicate that the hypervalent iodine(III) reagent acts as a conventional Lewis acid, such as $SnCl_4$, and $BF_3 \cdot OEt_2$, in the reaction with the 2,3-epoxy alcohol derivatives.[2]

On the other hand, *cis*-2,3-epoxy alcohols without protecting groups afforded ω-formylalkanoic acid derivatives from the bicyclic epoxy alcohols (Table 2, Entries 1 and 2) and β-hydroxy ketone from monocyclic epoxy alcohol (Table 2, Entry 3). Structures of (±)-**8,** (±)-**9**, and (±)-**6c**, were deduced from their spectral data and mechanistic considerations. The ω-formylalkanoic acid derivatives were supposed to be produced by tandem rearrangement followed by an oxidative ring cleavage (see Scheme 3). In contrast, when the rearranged product was β-hydroxy ketone, no further reaction occurred with PIFA (Table 2, Entry 3). The difference of the results between entries 1, 2 and entry 3 might be due to the difference of the ring systems, five-membered and six-membered ring on which the oxirane rings and

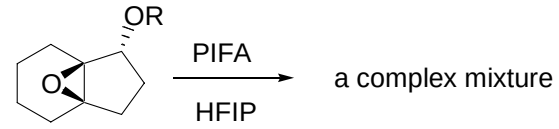
Table 2. Reaction of 2, 3-epoxy alcohol derivatives with PIFA[a]

Entry	Substrate	Product	Yield (%)[b]
1	 (±)-*cis*-**1c**	 (±)-**8**	57
2	 (±)-*cis*-**2c**	 (±)-**9**	63
3	 (±)-*cis*-**3c**	 (±)-**6c**	98

[a]Reactions were carried out with Substrate (1 equiv.) and PIFA (1 equiv.) in HFIP. [b]Isolated yields.

hydroxyl groups exist. It was difficult to form the chelation structure shown in the first step of Scheme 3 in six membered ring system, and PIFA played like $BF_3 \cdot OEt_2$ in entry 3 (cf. see ref. 2e).

The stereochemistry of the epoxy alcohol derivatives is also critical to this reaction. As shown above, *cis*-epoxy benzyl ether ((±)-***cis*-1a**) and *cis*-epoxy benzoates ((±)-***cis*-1b**) afforded the rearranged products ((±)-**4a**) and ((±)-**4b**) (Table 1)**,** and the *cis*-epoxy alcohol (***cis*-1c)** afforded the ω-formylalkanoic acid ((±)-**8)** in moderate to good yields (Table 2). In contrast, the *trans*-epoxy benzyl ether ((±)-***trans*-1a**), *trans*-epoxy benzoate ((±)-***trans*-1b**) and *trans*-epoxy alcohol ((±)-***trans*-1c**) afforded a complex mixture (Scheme 2).

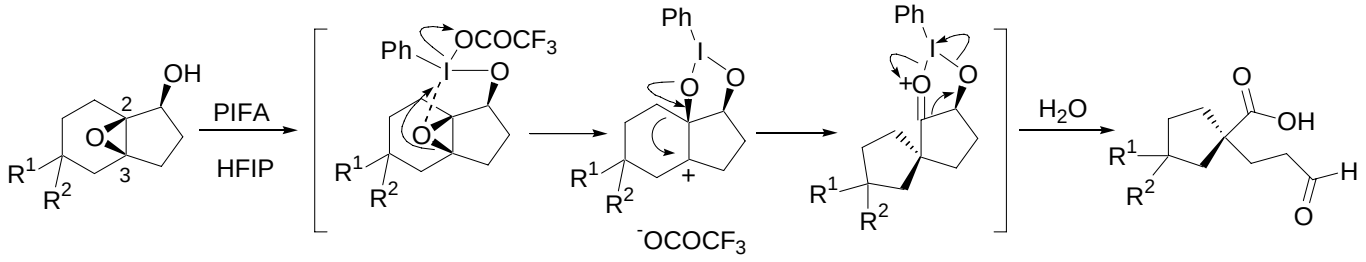


(±)-*trans*-1a,b,c

(**a**: R=$C_6H_5CH_2$, **b**: R=C_6H_5CO, **c**: R=H)

Scheme 2.

Judging from the fact that *trans*-epoxy alcohol derivatives gave poor results, PIFA seemed to act by coordination to two oxygens, which are from the alcohol (or its benzyl ether and benzoyl ester) and the oxyrane ring. Then, a plausible reaction mechanism of the tandem reaction in Table 2 was envisaged as shown in Scheme 3. PIFA first coordinates to the oxgen atoms of the alcohol and oxirane ring. The alkyl group of the ring then migrates to the generated C3 carbocation. Finally, the oxidative ring cleavage of the diol moiety is caused by PIFA to afford the ω-formylalkanoic acid derivatives.[7]

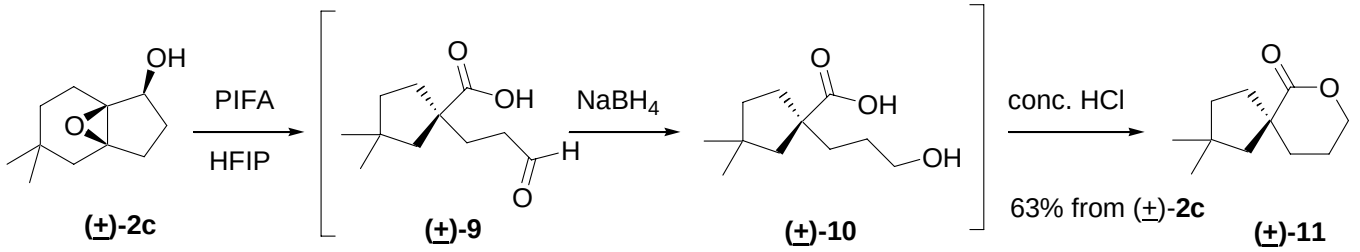


Scheme 3. Tandem rearrangement and oxidative ring cleavage reaction of bicyclic 2, 3-epoxy alcohol

As a result, the one-pot transformation from the 2,3-epoxy alcohols to ω-formylalkanoic acids was achieved only using PIFA. Tandem reactions, in other words, the domino or cascade reactions, in general, have attracted much attention in organic synthesis because of their efficiency and applicability. Furthermore, tandem reactions[8] including the rearrangements of 2,3-epoxy alcohols and their derivatives

have been reported during the past several years.[9]

This tandem rearrangement and subsequent oxidative cleavage reaction is useful for synthesizing lactone in one-pot operation. As shown in Scheme 4, bicyclic 2,3-epoxy alcohol could be converted into spirocyclic lactone by a simple one-pot procedure. ω-Formylalkanoic acid ((±)-**9),** which was produced by the reaction shown in Scheme 3, was treated with $NaBH_4$ and conc. HCl, subsequently. As a result, reduction of formyl group leading to hydroxyl carboxylic acid ((±)-**10**) and formation of lactone occurred smoothly to give spirocyclic lactone ((±)-**11**) (Scheme 4).



Scheme 4. One-pot transformation of 2,3-epoxy alcohol to spirocyclic lactone

In summary, we have found an unprecedented tandem rearrangement and oxidative ring cleavage reaction of 2,3-epoxy alcohol derivatives using the hypervalent iodine(III) reagent. This reaction clearly shows the interesting double reactivity of the hypervalent iodine(III) reagent which includes the oxidation activity and Lewis acidity. Further studies of this reaction and its application are currently in progress in our laboratory.

EXPERIMENTAL

All melting points are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded at 300 and 75 MHz respectively with $CDCl_3$ as a solvent and $SiMe_4$ as an internal standard. IR spectra (cm^{-1}) were recorded as KBr pellets. PIFA is commercially available. $(CF_3)_2CHOH$ was obtained from commercial suppliers and were used without further purification. The spectral data of the compounds ((±)-**4b,** (±)-**5b,** (±)-**6b,** (±)-**7**) were identical with those already reported by us.[2a]

Preparation of Epoxy Alcohol Derivatives. The *cis*-epoxy alcohols ((±)-***cis*-1c, 2c)**, *cis*-epoxy benzoates ((±)-***cis*-1b**, **2b**, **3b)** and *trans*-epoxy benzoate ((±)-***trans*-1b)** were prepared by the literature procedures[2a] reported by us. **3c** was prepared from the corresponding α,β-unsaturated ketone,[10] synthesized by the literature procedures, in a two-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 literarure procedures.[11] *cis*-Benzyl ether

((±)-***cis*-1a, 2a,** and **3a**) were prepared by benzylation of the corresponding epoxy alcohols with benzyl bromide and NaH in THF-DMF (4 : 1) at 0 °C. (±)-***trans*-1c** was prepared by hydrolysis of (±)-***trans*-1b**. (±)-***trans*-1a** was prepared by benzylation of (±)-***trans*-1c** as already described above.

(±)-*cis*-1,6-Epoxy-7-benzyloxybicyclo[4.3.0]nonane ((±)-*cis*-1a): colorless crystals; mp 73.5 °C (hexane-AcOEt); IR (KBr) cm^{-1}: 698, 741, 1099, 1454; ^{1}H-NMR ($CDCl_3$) δ: 1.20-2.08 (12H, m), 3.90 (1H, t, *J* = 8.1 Hz), 4.53 (1H, A in ABq, *J* = 12.3 Hz), 4.65 (1H, B in ABq, *J* = 12.3 Hz), 7.26-7.38 (5H, m); ^{13}C-NMR ($CDCl_3$) δ: 19.9 (2C), 24.7, 24.8, 26.7, 29.4, 64.1, 66.0, 71.1, 82.3, 127.5, 127.6 (2C), 128.3 (2C), 138.7; *Anal.* Calcd for $C_{16}H_{20}O_2$: C; 78.65; H, 8.25. Found: C, 78.84; H, 8.09.

(±)-*trans*-1,6-Epoxy-7-benzyloxybicyclo[4.3.0]nonane ((±)-*trans*-1a): colorless oil; IR (KBr) cm^{-1}: 696, 735, 1070, 1437; ^{1}H-NMR ($CDCl_3$) δ: 1.19-2.10 (11H, m), 2.25 (1H, m), 3.90 (1H, d, *J* = 5.1 Hz), 4.44 (1H, A in ABq, *J* = 12.0 Hz), 4.60 (1H, B in ABq, *J* = 12.0 Hz), 7.23-7.40 (5H, m); ^{13}C-NMR ($CDCl_3$) δ: 20.2, 20.5, 22.1, 26.3, 26.4, 29.9, 66.9, 67.3, 71.3, 81.1, 127.4 (3C), 128.2 (2C), 138.4. *Anal.* Calcd for $C_{16}H_{20}O_2$: C; 78.65; H, 8.25. Found: C, 78.74; H, 8.31.

(±)-*trans*-1,6-Epoxybicyclo[4.3.0]nonan-7-ol ((±)-*trans*-1c): colorless oil; IR (KBr) cm^{-1}; 3385; ^{1}H-NMR ($CDCl_3$) δ: 1.17-2.32 (13H, m), 4.17 (1H, d, *J* = 5.1 Hz); ^{13}C-NMR ($CDCl_3$) δ: 20.0, 20.6, 21.7, 26.4, 29.4, 30.4, 67.1, 67.6, 74.1; *Anal.* Calcd for $C_9H_{14}O_2$: C; 70.10, H, 9.15. Found: C, 70.14; H, 9.14.

(±)-*cis*-1,6-Epoxy-7-benzyloxy-3,3-dimethylbicyclo[4.3.0]nonane ((±)-*cis*-2a): colorless crystals; mp 56 °C (hexane); IR (KBr) cm^{-1}: 698, 743, 1099, 1454; ^{1}H-NMR ($CDCl_3$) δ: 0.77 (3H, s), 0.89 (3H, s), 1.09 (1H, m), 1.31-1.50 (4H, m), 1.65-1.85 (3H, m), 2.06 (1H, m), 2.22 (1H, m), 3.90 (1H, t, *J* = 7.5 Hz), 4.55 (1H, A in ABq, *J* = 12.3 Hz), 4.66 (1H, B in ABq, *J* = 12.3 Hz), 7.26-7.38 (5H, m); ^{13}C-NMR ($CDCl_3$) δ: 21.9, 25.3, 25.9, 28.6, 30.5, 30.7, 31.9, 40.2, 64.2, 65.4, 71.1, 82.1, 127.5 (3C), 128.3 (2C), 138.7; *Anal.* Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.41; H, 8.82.

(±)-*cis*-1-Benzyloxy-2-butyl-2,3-epoxy-3-methylcyclohexane ((±)-*cis*-3a): colorless oil; IR (KBr) cm^{-1}: 698, 735, 1072, 1094, 1454; ^{1}H-NMR ($CDCl_3$) δ: 0.85 (3H, t, *J* = 6.9 Hz), 1.22-1.32 (4H, m), 1.30 (3H, s), 1.54-1.66 (6H, m), 1.85 (1H, m), 2.15 (1H, m), 3.72 (1H, t, *J* = 6.9 Hz), 4.48 (1H, d, *J* = 12.3 Hz), 4.70 (1H, d, *J* = 12.3 Hz), 7.26-7.39 (5H, m); ^{13}C-NMR ($CDCl_3$) δ: 14.0, 18.9, 20.8, 23.0, 24.6, 27.6, 29.8, 30.3, 63.2, 66.6, 70.2, 74.6, 127.5, 128.0, 128.2, 138.8; *Anal.* Calcd for $C_{18}H_{26}O_2$: C; 78.79; H, 9.55. Found: C, 78.93; H, 9.58.

(±)-*cis*-2-Butyl-2,3-epoxy-3-methylcyclohexan-1-ol ((±)-*cis*-3c): colorless oil; IR (KBr) cm^{-1}: 3439; ^{1}H-NMR ($CDCl_3$) δ: 0.92 (3H, t, *J* = 6.9 Hz), 1.16-1.67 (13H, m), 1.90-2.21 (3H, m), 3.93 (1H, m); ^{13}C-NMR ($CDCl_3$) δ: 14.0, 15.5, 20.1, 23.0, 27.3, 31.2, 31.3, 31.6, 65.6, 66.6, 67.4; *Anal.* Calcd for $C_{11}H_{20}O_2$: C; 71.70; H, 10.94. Found: C, 71.73; H, 10.84.

General Procedure for the Rearrangement Reaction of 2,3-Epoxy Benzyl Ether or 2,3-Epoxy Benzoate with PIFA (Table 1). To a stirred solution of the substrate (1 mmol) in 1, 1, 1, 3, 3,

3-hexafluoro-2-propanol (10 mL) was added PIFA (473 mg, 1.1 mmol) at 0 °C under N_2 atmosphere. Stirring was continued for 12 h at 0 °C to rt. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ 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 (25/1 ~ 15/1) as the eluent to give the rearranged products in the yields shown in Table 1.

General Procedure for the Rearrangement Reaction of 2,3-Epoxy Benzyl Ether or 2,3-Epoxy Benzoate with BF_3·Et_2O (Table 1). To a stirred solution of the substrate (1 mmol) in CH_2Cl_2 (10 mL) was added BF_3·Et_2O (0.14 mL, 1.1 mmol) at 0 °C under N_2 atmosphere. Stirring was continued until the completion of the reaction (TLC check). The reaction mixture was quenched with saturated aqueous $NaHCO_3$ 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 (25/1 ~ 15/1) as the eluent to give the rearranged products in the yields shown in parentheses in Table 1.

(±)-**2-Benzyloxy-1-oxospiro[4.4]nonane ((±)-4a):** colorless oil; IR (KBr) cm^{-1}: 1738; ^{1}H-NMR ($CDCl_3$) δ: 1.34-1.96 (11H, m), 2.20 (1H, m), 3.88 (1H, dd, *J* = 7.5, 9.3 Hz), 4.70 (1H, A in ABq, *J* = 12 Hz), 4.84 (1H, B in ABq, *J* = 12 Hz), 7.25-7.40 (5H, m); ^{13}C-NMR ($CDCl_3$) δ: 25.5, 25.7, 27.3, 33.0, 37.5, 38.4, 54.5, 72.0, 80.2, 127.7, 128.0 (2C), 128.4 (2C), 137.8, 220.9; HRMS (FAB) Calcd for $C_{16}H_{21}O_2$ $[M+H]^+$: 245.1541. Found: 245.1552.

(±)-**2-Benzyloxy-7,7-dimethyl-1-oxospiro[4.4]nonane ((±)-5a):** colorless oil; IR (KBr) cm^{-1}: 1738; ^{1}H-NMR ($CDCl_3$) δ: 1.05 (3H, s), 1.08 (3H, s), 1.33-2.21 (10H, m), 3.85 (1H, t), 4.68 (1H, A in ABq, *J* = 12 Hz), 4.83 (1H, B in ABq, *J* = 12 Hz), 7.28-7.41 (5H, m); HRMS (FAB) Calcd for $C_{18}H_{24}O_2Na$ $[M+Na]^+$: 295.1674. Found: 295.1679.

(±)-***cis*-1-Benzyloxy-2-methyl-2-pentanoylcyclopentane ((±)-6a):** colorless oil; IR (KBr) cm^{-1}: 1703; ^{1}H-NMR ($CDCl_3$) δ: 0.89 (3H, t, *J* = 7.5 Hz), 1.20-1.34 (2H, m), 1.23 (3H, s), 1.48-1.75 (6H, m), 1.92-2.04 (2H, m), 2.39-2.57 (2H, m), 4.14 (1H, t, *J* = 6.6 Hz), 4.42 (1H, A in ABq, *J* = 12 Hz), 4.53 (1H, B in ABq, *J* = 12 Hz), 7.25-7.33 (5H, m); ^{13}C-NMR ($CDCl_3$) δ: 13.9, 17.6, 20.3, 22.4, 26.1, 30.1, 35.0, 37.5, 58.1, 71.7, 82.8, 127.4, 127.5 (2C), 128.3 (2C), 138.8, 214.7; *Anal.* Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.64; H, 9.68.

General Procedure for the Reaction of 2,3-Epoxy Alcohols with PIFA (Table 2). To a stirred solution of the substrate ((±)-***cis*-1c,** (±)-***cis*-2c,** (±)-***cis*-3c**) (1 mmol) in 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol (10 mL) was added PIFA (430 mg, 1 mmol) at 0 °C under N_2 atmosphere. Stirring was continued for 30 min at 0 °C to rt. The reaction mixture was concentrated in vacuo. The residue was purified by SiO_2 column chromatography using hexane-AcOEt (5/1 ~ 2/1) as the eluent to give the products in yields shown in Table 2.

(±)-**1-(3-Oxopropyl)cyclopentanecarboxylic acid ((±)-8):** colorless oil; IR (KBr) cm^{-1}: 1697, 1724, 3074. ^{1}H-NMR ($CDCl_3$) δ: 1.15-2.69 (12H, m), 9.78 (1H, s), 10.05 (1H, s); HRMS (FAB) Calcd for $C_9H_{15}O_3$ $[M+H]^+$: 171.1021. Found: 171.1017.

(±)-**3,3-Dimethyl-1-(3-Oxopropyl)cyclopentanecarboxylic acid ((±)-9):** colorless oil; IR (KBr) cm^{-1}: 1693, 1728, 3062; ^{1}H-NMR ($CDCl_3$) δ: 1.03 (3H, s), 1.05 (3H, s), 1.38 (1H, d, *J* = 13.5 Hz), 1.43-1.71 (4H, m), 1.99 (2H, t, *J* = 7.9 Hz), 2.13 (1H, d, *J* = 13.5 Hz), 2.29 (1H, m), 2.48 (2H, t, *J* = 7.7 Hz), 9.77 (1H, s); ^{13}C-NMR ($CDCl_3$) δ: 29.2, 30.1, 32.1, 35.3, 39.4, 40.4, 40.7, 50.2, 53.3, 184.0, 201.6; HRMS (FAB) Calcd for $C_{11}H_{19}O_3$ $[M+H]^+$: 199.1334. Found: 199.1326.

(±)-**(1*SR*,2*RS*)-2-Methyl-2-propanoylcyclopentananol ((±)-6c):** colorless oil; IR (KBr) cm^{-1}: 1693, 3441; ^{1}H-NMR ($CDCl_3$) δ: 0.91 (3H, t, *J* = 6.9 Hz), 1.16 (3H, s), 1.20-1.36 (2H, m), 1.49-2.02 (8H, m), 2.16 (1H, brs), 2.41-2.56 (2H, m), 4.29 (1H, t, *J* = 8.1 Hz); ^{13}C-NMR ($CDCl_3$) δ: 13.9, 16.7, 18.3, 22.3, 25.7, 30.2, 32.8, 37.7, 57.1, 75.5, 216.7; *Anal.* Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.47; H, 10.83.

Transformation of 2, 3-Epoxy Alcohol to Spirocyclic Lactone (Scheme 4). To a stirred solution of the substrate ((±)-**2c**) (40.3 mg, 0.221 mmol) in 1, 1, 1, 3, 3, 3-hexafuluoro-2-propanol (2.2 mL) was added PIFA (104.7 mg, 0.244 mmol) at 0 ℃ under N_2 atmosphere. After stirring was continued for 30 min at 0 ℃, $NaBH_4$ (83.7 mg, 2.21 mmol) was added and the mixture was gradually warmed to rt. After being stirred for 1.5 h, concentrated aqueous HCl (0.5 mL) was added at 0 ℃ and the solution was stirred for an additional 1 h. H_2O was added to the reaction mixture, which was extracted with CH_2Cl_2. 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 (±)-**11** (25.3 mg, 63%).

(±)-**2,2-Dimethyl-7-oxaspiro[4.5]decan-6-one ((±)-11):** colorless oil; IR (KBr) cm^{-1}: 1094, 1148, 1730; ^{1}H-NMR ($CDCl_3$) δ: 1.06 (3H, s), 1.11 (3H, s), 1.45 (1H, d, *J* = 13.4 Hz), 1.54 (1H, m), 1.64-1.76 (2H, m), 1.82-1.95 (4H, m), 2.12 (1H, d, *J* = 13.4 Hz), 2.33 (1H, m), 4.29-4.38 (2H, m); ^{13}C-NMR ($CDCl_3$) δ 21.1, 29.2, 30.0, 35.0, 38.6, 39.9, 40.7, 49.8, 53.0, 69.5, 177.7; HRMS (EI) Calcd for $C_{11}H_{18}O_2$: 182.1307. Found: 182.1308.

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