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Regio- and Stereoselective Rearrangement Reactions of Various α,β-Epoxy Acylates: Suitable Combination of Acyl Groups and Lewis Acids

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Abstract: Regio- and stereoselective rearrangement reactions of various α,β-epoxy acylates including acyclic, monocyclic and bicyclic systems occurred under a suitable combination of acyl groups (benzoyl, *p*-nitrobenzoyl, camphanoyl) and Lewis acids (BF_3•Et_2O, MABR).

Introduction

Although acyl groups are used as very useful protecting groups of alcohol functionalities and are also known as functional groups which tend to produce neighboring group participation in many types of reactions, the occurrence of the regio- and stereoselective rearrangement reactions using their electron-withdrawing nature is rare.[1] Recently, we found that the Lewis acid treatment of bicyclic *cis*-α,β-epoxy acylates (acetate and benzoate) afforded the spiro compounds by cleavage of the oxirane ring at the β-position of the acyloxy group due to its inducing effect, followed by successive rearrangement of the carbon skeleton.[2] This rearrangement reaction proved to be useful for the construction of a variety of spirocyclane systems and quaternary carbon centers on rings and for the syntheses of their optically active forms.[3] However, the success of this reaction was governed by the stereochemistries of the substrates. Namely, the cyclic *cis*-epoxy acylates afforded the rearranged products in good yields, whereas the *trans*-ones having acetyl and benzoyl moieties gave unsuccessful results because of the neighboring group participation of the acyloxy groups. Suppression of this neighboring group participation is strongly desirable in order to make this rearrangement reaction applicable to the *trans*-ones. We then examined this rearrangement in detail, and communicated the remarkable effects of acyloxy groups and an exceptionally bulky Lewis acid, methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR).[4] Namely, an acyloxy group such as a strong electron-withdrawing *p*-nitrobenzoyl group, a very bulky camphanoyl group and a bulky Lewis acid, MABR, made the rearrangement applicable not only to cyclic *trans*-derivatives but also to acyclic ones.[5]

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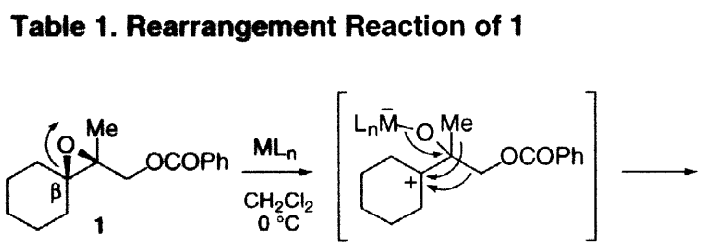
During a series of studies, we focused on these remarkable effects (steric and electrostatic) of acyl groups and the exceptionally bulky Lewis acid, MABR. We then examined additional acyclic tetrasubstituted derivatives and monocyclic tetra- and trisubstituted ones in detail, and found that a suitable combination of an acyl group and Lewis acid makes the rearrangement reaction successful with high yields and with high selectivities in various systems. We also succeeded in determining the general tendency of the appropriate combination of acyl groups and Lewis acids in acyclic, monocyclic and bicyclic systems. In this paper, we describe the full details of our work connected with the rearrangement reaction of various epoxy acylates.

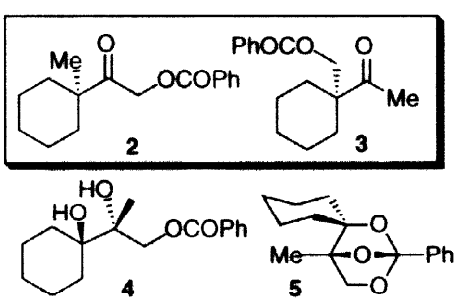
Results and Discussion

Rearrangement of Acyclic α,β-Epoxy Acylates

Tetrasubstituted Systems: We initially examined a Lewis acid using racemic **1** as the substrate in CH_2Cl_2 at 0°C (Table 1). No rearranged product was obtained along with the diol **4** and orthoester **5** in the cases of representative Lewis acids such as BF_3•Et_2O, $Al(OC_6F_5)_3$, [6] $TiCl_4$, $SnCl_4$, etc. This is due to the formation of the dioxycarbenium ion intermediate **A** by the neighboring group participation of an acyl group.[7] However, the use of MABR gave two types of rearranged products **2** formed by the migration of a methyl group and **3** formed by the migration of an acyloxymethyl group *via* regioselective cleavage of an oxirane ring at the β-position due to the electron-withdrawing nature of the acyl groups.

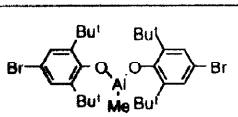
Table 1. Rearrangement Reaction of 1

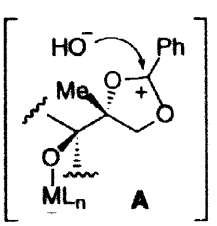




ML_n	Yield (%) 2	3	4	5
MABR[a]	4	40	9	-
BF_3·Et_2O	-	-	60	22
$Al(OC_6F_5)_3$, $TiCl_4$ / $EtAlCl_2$, $SnCl_4$	-	-	24~89	-

[a] MABR=



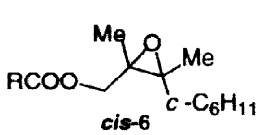
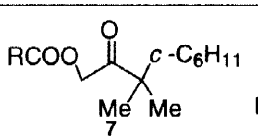
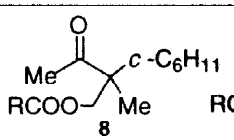
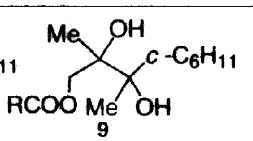
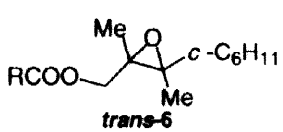
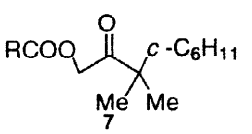
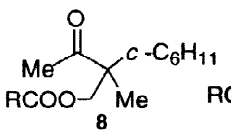
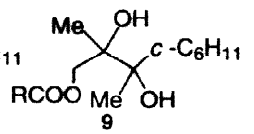


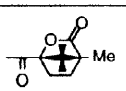
The same tendency was observed in the case of racemic *cis*-**6** (Table 2).[8] Although the acyclic α,β-epoxy benzoate (*cis*-**6a**) afforded the diol **9a** using BF_3•Et_2O (entry 1), the use of MABR predominantly afforded the rearranged products (**7a** and **8a**) in good yields. Thus, *cis*-**6a-c** afforded **7a-c**, formed by the migration of a methyl group, predominantly along with minor **8a-c**, which was formed by the migration of an acyloxymethyl group (entries 2-4). *trans*-**6a**, **b** predominantly afforded **8a**, **b** (entries 6 and 7). But, to our surprise, *trans*-**6c** having a camphanoyloxy group predominantly afforded **7c** (entry 8).

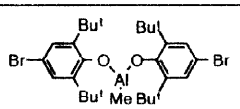
For the rearrangement reactions, the migratory aptitude of alkyl groups having an electron-withdrawing group are generally low.[9] For that reason, the yield of **8b** was lower than **8a** in both cases of *cis*-**6a, b** and *trans*-**6a, b** (entries 2, 3 and 6,7). It is noteworthy that the migration of the acyloxymethyl group took priority over the migration of the methyl group using a suitable combination of an acyl group and a Lewis acid in *trans*-**6a,b** (entries 6 and 7). The differences in the selectivity between *cis*-**6** and *trans*-**6**, in other words, the ratio of **7** and **8**, occurred during the coodination stage of MABR with the epoxide. In the cases of *cis*-**6a-c**, the β-side of the epoxide in Figure 1 (*cis*) is not crowded compared to the α-side, therefore, MABR coordinates with the oxirane ring from this side and cleaves the oxirane ring at the β-position of the acyloxy group. The repulsion between the MABR ligand and the methyl group accelerates migration of the methyl group and **7a-c** were predominantly produced.[4] On the other hand, in the cases of *trans*-**6a, b** there is little difference in the spaces around the epoxide so that low selectivity appeared (Figure 1, *trans*T-1 and/or *trans*T-2), and in the case of *trans*-**6c**, MABR coordinates with the oxirane ring from the α-side because of the bulkiness of the camphanoyl group so that selectivity was reversed for *trans*-**6a, b** (Figure 1, *trans*T-2).

Table 2. Reaction of Tetrasubstituted Acyclic Epoxy Acylates

Acyl Groups of the Products, **a**: R=Ph; **b**: R=*p*-NO_2Ph; **c**: COR=(-)-Camphanoyl[a]

Entry	Substrate	Lewis Acid	Rearranged Product (Yield)		Other Products (Yield)
	 *cis*-**6**		 **7**	 **8**	 **9**
1	**a**; R=Ph	BF_3•Et_2O	-	-	**9a** (54%)
2	**a**; R=Ph	MABR[b]	**7a** (58%)	**8a** (12%)	-
3	**b**; R=*p*-NO_2Ph		**7b** (73%)	**8b** (6%)	-
4	**c**; COR=(-)-camphanoyl		**7c** (82%)	**8c** (11%)	-
	 *trans*-**6**		 **7**	 **8**	 **9**
5	**a**; R=Ph	BF_3•Et_2O	-	-	**9a** (30%)
6	**a**; R=Ph	MABR	**7a** (10%)	**8a** (52%)	-
7	**b**; R=*p*-NO_2Ph		**7b** (23%)	**8b** (49%)	-
8	**c**; COR=(-)-camphanoyl		**7c** (74%)	**8c** (16%)	-

[a] (-)-Camphanoyl= 

[b] MABR= 

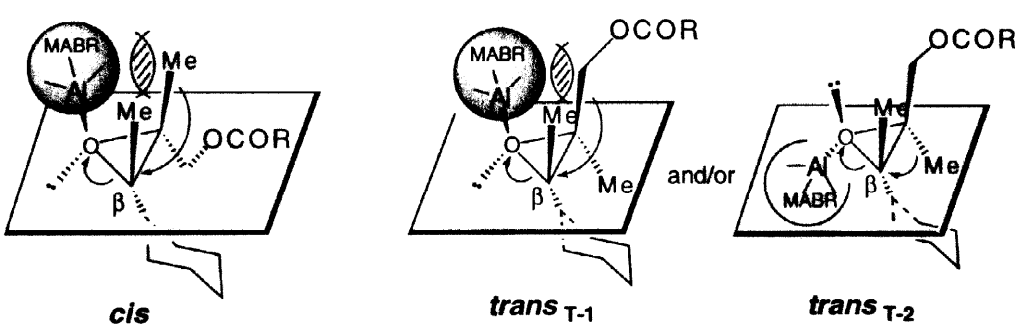
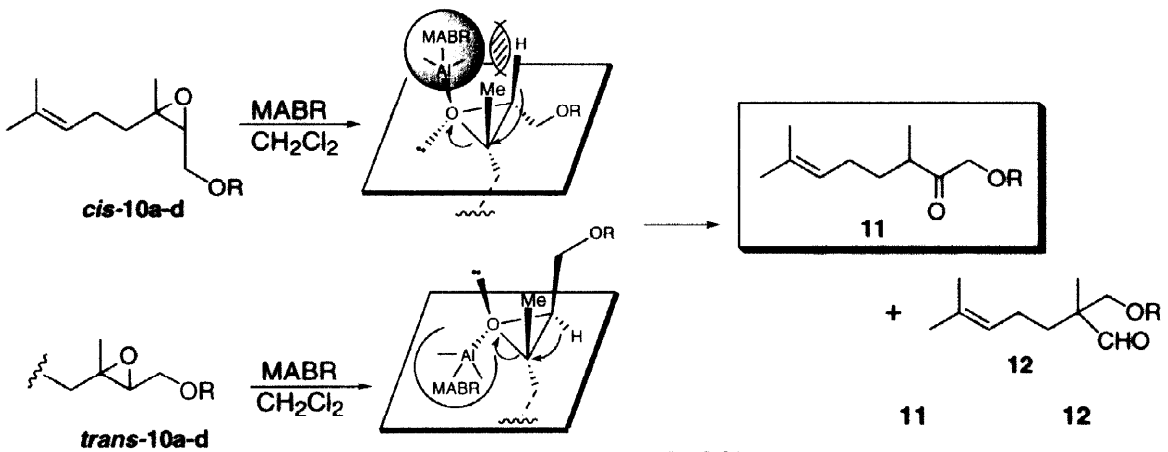


Figure 1

Trisubstituted Systems: [5] A characteristic feature of our rearrangement reaction using an electron-withdrawing acyl group is exemplified by the following experiments (Scheme 1).[8] Thus, treatment of trisubstituted epoxy acylates, *cis*-**10a-c** and *trans*-**10a-c**, with MABR afforded **11a-c** in good yields, by hydride migration and no **12a-c**. These results are in striking contrast with Yamamoto's results,[10] in which the reactions of epoxides, *cis*-**10d** and *trans*-**10d**, having an electron-donating silyl ether (TBS: *tert*-butyldimethylsilyl) with MABR selectively afforded β-siloxy aldehydes **12d** and no **11d**. It is noteworthy that a change in the protecting group of an alcohol can control the migratory nature of the substituents.



		11	12
cis-10	**a** (R= PhCO)	70%	0%
	b (R= *p*-NO_2PhCO)	83%	0%
	c (R= (-)-camphanoyl)	91%	0%
	d (R= TBS)	0%	98%[a]
trans-10	**a** (R= PhCO)	48%	0%
	b (R= *p*-NO_2PhCO)	76%	0%
	c (R= (-)-camphanoyl)	81%	0%
	d (R= TBS)	0%	99%[a]

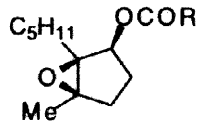
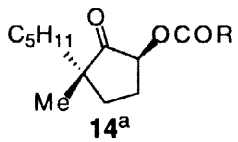
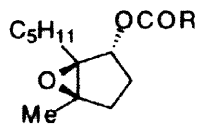
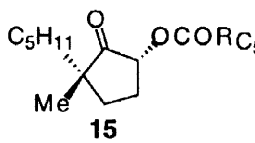
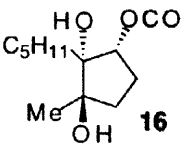
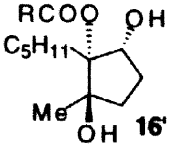
Scheme 1

[a] see ref 10

Rearrangement of Cyclic α,β-Epoxy Acylates

Tetrasubstituted 5-Membered Systems: [5] We next examined the application of these rearrangement reactions to monocyclic systems. We examined the suitable combination of an acyl group and a Lewis acid using tetrasubstituted **13** (Table 3).[8] Although *cis*-**13a-c** afforded the rearranged products (**14a-c**) in good yields using BF_3•Et_2O (entries 1-3),[3] the reaction did not proceed at all with the use of MABR (entry 4). On the other hand, *trans*-**13a** with a benzoyl group gave a 92% yield of the diols (**16a** and **16'a**) with no rearranged product because of the neighboring group participation of the benzoyl group (entry 5). However, *trans*-**13c** with a camphanoyl group afforded the rearranged product **15c** (56%) due to the efficient suppression of the neighboring group participation (entry 6). The use of a bulky Lewis acid, MABR, in *trans*-**13c** gave 83% yield of the rearranged product in combination with the bulky camphanoyl functionality (entry 7). These results are rationalized as follows. The oxirane ring of the *cis*-derivatives are very congested so that the bulky Lewis acid, MABR, could not coordinate with it (entry 4). On the other hand, that of the *trans*-ones is not congested compared to the *cis*-ones so that bulky MABR could approach the oxirane ring and the rearrangement reaction proceeded well (entry 7).

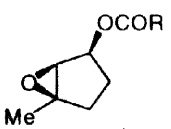
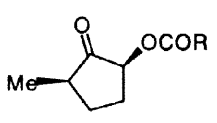
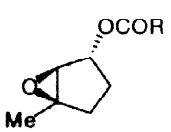
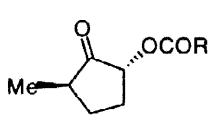
Table 3. Reaction of Tetrasubstituted 5-Membered Epoxy Acylates
Acyl Groups of the Products, **a**: R=Ph; **b**: R=*p*-NO_2Ph; **c**: COR=(-)-Camphanoyl

Entry	Substrate	Lewis Acid	Rearranged Product (Yield)	Other Products (Yield)	
	 *cis*-**13**[a]		 **14**[a]		
1	**a**; R= Ph	BF_3•Et_2O	**14a** (61%)		
2	**b**; R= *p*-NO_2Ph		**14b** (73%)		
3	**c**; COR= (-)-camphanoyl		**14c** (63%)		
4	**a**; R= Ph	MABR	no reaction		
	 *trans*-**13**		 **15**	 **16**	 **16'**
5	**a**; R= Ph	BF_3•Et_2O	-	**16a** (42%)	**16'a** (50%)
6	**c**; COR= (-)-camphanoyl		**15c** (56%)	**16c** (trace)	-
7	**c**; COR= (-)-camphanoyl	MABR	**15c** (83%)	-	-

[a] Spectroscopic data of *cis*-**13a,b** and **14a,b** are listed in ref 3.

Trisubstituted 5-Membered Systems: The trisubstituted 5-membered substrates were next examined (Table 4).[8] In these cases, a similar tendency was observed. The *cis*-derivatives (*cis*-**17a, b**) afforded the rearranged products **18a, b** in good yields by using BF_3•Et_2O (entries 1 and 2),[3] but the *trans*-ones tended to provide neighboring group participation and the rearranged products were obtained in low yields (entries 3 and 5). The effect of MABR was not observed in these systems (entries 4 and 6).

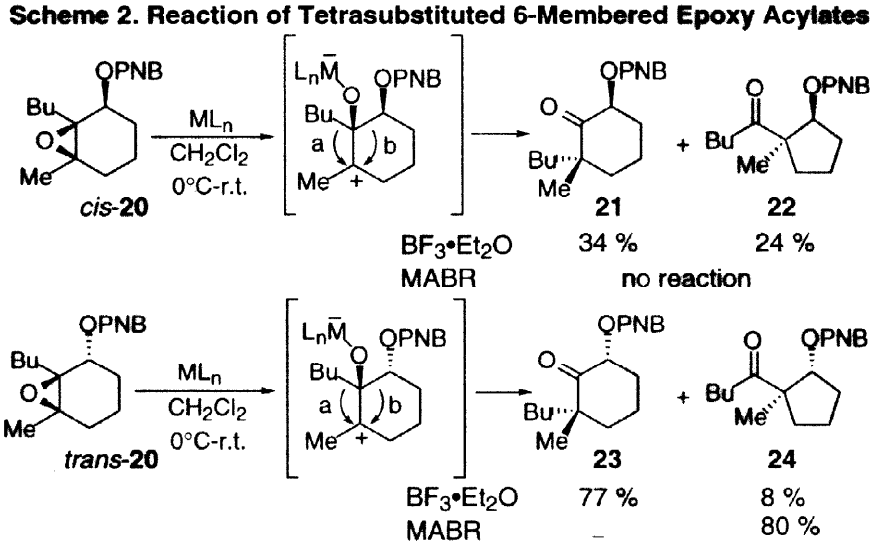
Table 4. Reaction of Trisubstituted 5-Membered Epoxy Acylates
Acyl Groups of the Products, **a**: R=Ph; **b**: R=*p*-NO_2Ph; **c**: COR=(-)-Camphanoyl

Entry	Substrate	Lewis Acid	Rearranged Product (Yield)
	 *cis*-**17**[a]		 **18**[a]
1	**a**; R= Ph	BF_3•Et_2O	**18a** (81%)
2	**b**; R= *p*-NO_2Ph		**18b** (79%)
	 *trans*-**17**		 **19**
3	**b**; R= *p*-NO_2Ph	BF_3•Et_2O	**19b** (22%)
4		MABR	complex mixture
5	**c**; COR= (-)-camphanoyl	BF_3•Et_2O	**19c** (47%)
6		MABR	**19c** (8%)

[a] Spectroscopic data of *cis*-**17a,b** and **18a,b** are listed in ref 3.

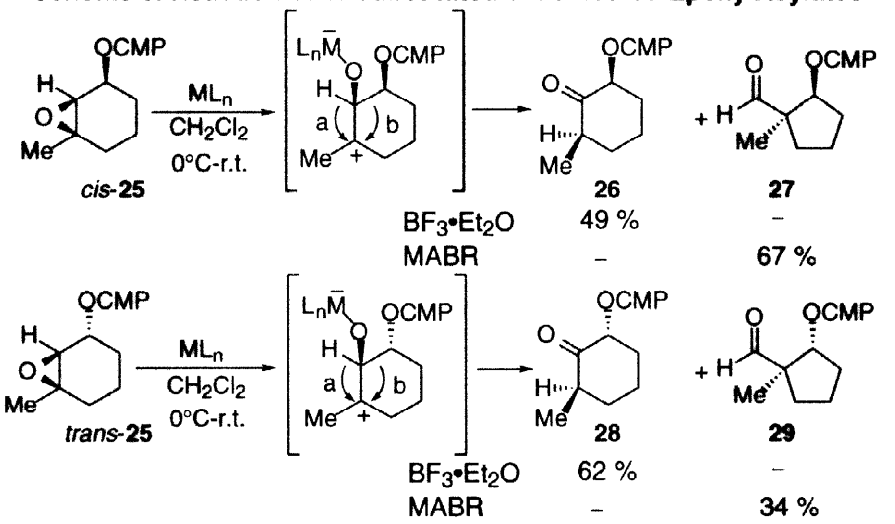
Tetrasubstituted 6-Membered Systems: We next examined the tetrasubstituted 6-membered α,β-epoxy acylates (*cis*- and *trans*-**20**).[8] In the cases of the 5-membered systems, contraction of the ring did not occur. This might be due to the unfavorable formation of the 4-membered ring. On the other hand, in the 6-membered system, it was thought that ring contraction competed with migration of the alkyl chain (route a or route b in Scheme 2). If we could control the reaction paths by the choice of acyl groups and Lewis acids, it would be an interesting result in the rearrangement reaction. The results are shown in Scheme 2. Although *cis*-**20** gave poor results,[3] *trans*-**20** showed fruitful results. The use of BF_3•Et_2O afforded **23** in high selectivity *via* route a and the use of MABR afforded **24** in good yield *via* route b with no **23**. With regard to the acyl groups, the *p*-nitrobenzoyl group gave the best results. Therefore, these results are now reported.

Scheme 2. Reaction of Tetrasubstituted 6-Membered Epoxy Acylates



Trisubstituted 6-Membered Systems: The trisubstituted ones are shown in Scheme 3.[8] In these systems, the same tendency as the tetrasubstituted 6-membered system was observed in both *cis*- and *trans*-**25**. The use of two types of Lewis acids (BF_3•Et_2O and MABR) can control reaction paths a and b. The use of BF_3•Et_2O afforded **26** and **28**, formed by the migration of a hydride (route a), with no **27** and **29**, formed by the ring contraction (route b). On the other hand, the use of MABR afforded **27** and **29** with no **26** and **28**. With regard to the acyl groups, the camphanoyl group gave the best results.

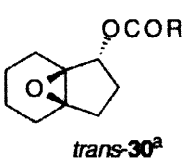
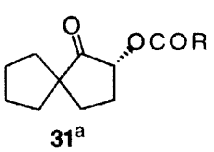
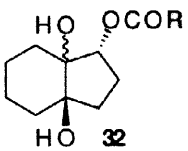
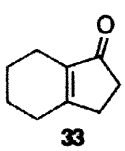
Scheme 3. Reaction of Trisubstituted 6-Membered Epoxy Acylates



Bicyclic Systems:[2,3,5] The *trans*-**30** was examined as the substrate (Table 5).[8] We already found and reported that the treatment of the *cis*-derivatives with BF_3•Et_2O gave the rearranged products in good yields. However, treatment of *trans*-**30a** gave a small amount of rearranged product **31a** along with the diols **32a** and the enone **33** when using the benzoyl group as the acyl group (entry 1). The use of a *p*-nitrobenzoyl group dramatically increased the yield of the rearranged product (entry 2). The use of a bulky camphanoyl group also gave the desired product in good yield (entry 3) because of the same reason as the monocyclic systems.[5] We next examined the bulky Lewis acid, MABR. The *p*-nitrobenzoate derivative, *trans*-**30b**, afforded the rearranged product **31b** in 24 % yield (entry 4), and the camphanoate one, *trans*-**30c** afforded the diol **32c** with no **31c** (entry 5). The differences in the reactivity should depend on the size of the Lewis acid; bulky MABR could not sufficiently coordinate with epoxide, which is located on the crowded position. These results also imply the importance of the suitable combination of acyl groups and Lewis acids.

Table 5. Reaction of Bicyclic Epoxy Acylates

Acyl Groups of the Products, **a**: R=Ph; **b**: R=*p*-NO_2Ph; **c**: COR=(-)-Camphanoyl

Entry	Substrate	Lewis Acid	Rearranged Product (Yield)	Other Products (Yield)	
	 *trans*-**30**[a]		 **31**[a]	 **32**	 **33**
1	**a**; R=Ph	BF_3•Et_2O	**31a** (18%)	**32a**(65%)	(trace)
2	**b**; R=*p*-NO_2Ph		**31b** (63%)	**32b** (trace)	(20%)
3	**c**; COR=(-)-camphanoyl		**31c** (65%)	**32c** (trace)	(6%)
4	**b**; R=*p*-NO_2Ph	MABR	**31b** (24%)	-	(67%)
5	**c**; COR=(-)-camphanoyl		-	**32c** (60)	-

[a] Spectroscopic data of *trans*-**30a** and **31a-c** are listed in ref 3.

Consideration for the Suitable Combination of Acyl Groups and Lewis Acids

As already mentioned, we have now found that the suitable combination of acyl groups and Lewis acids is important in the rearrangement reactions. The summary is showed in Table 6. Concerning the Lewis acids, the confomation becomes more rigid from the acyclic substrate to monocyclic and bicyclic ones, and the size of the preferable Lewis acid becomes smaller from MABR to BF_3•Et_2O. Especially, the effect of MABR is remarkable in the acyclic systems. The bulkiness of MABR is thought to efficiently suppress the neighboring group participation of an acyl group. Monocyclic systems are located in the middle. Both MABR and BF_3•Et_2O are equally effective. Especially, we could control the reaction paths in the cases of the 6-membered systems. Concerning the acyl groups, an apparent tendency was observed. Three types of acyl groups (benzoyl, *p*-nitrobenzoyl, camphanoyl) are equally effective in acyclic systems and *cis*-cyclic systems (monocyclic and bicyclic ones). The benzoyl group is not useful at all in the *trans*-ones so that a strong electron-withdrawing *p*-nitrobenzoyl, and a very bulky camphanoyl group allow the successful rearrangement reaction even from the *trans*-ones.

Table 6. Suitable Combination of Acyl Groups and Lewis Acids

Substrate type			Preferable Lewis acid	Preferable Acyl Group
Acyclic Systems			MABR	Almost all acyl groups (Bz, PNB, CMP)
Monocyclic Systems	5-Membered Systems	*cis*	BF_3·Et_2O	Almost all acyl groups
		trans	BF_3·Et_2O ≒ MABR	CMP > PNB ≫ Bz
	6-Membered Systems	*cis*	//	Almost all acyl groups
		trans	//	CMP, PNB
Bicyclic Systems		*cis*	BF_3·Et_2O	Almost all acyl groups
		trans	BF_3·Et_2O	CMP ≒ PNB ≫ Bz

PNB= *p*-NO_2PhCO, CMP= (-)-camphanoyl

Conclusion

We have examined our rearrangement reaction of various α,β-epoxy acylates [acyclic, monocyclic (5-membered, 6-membered) and bicyclic ones] in detail, and the successful rearrangement was achieved by controlling the electron-withdrawing nature of the acyl groups by a suitable combination of acyl groups and Lewis acids. All acyl groups used in this article are easily protected or deprotected.[11] The corresponding acylation reagents are easily available and not expensive. All epoxy acylates are stable for air at room temperature. Furthermore, the present reactions are applicable to the syntheses of their optically active forms, chiral spirocyclane systems[12-15] and chiral quaternary carbon centers[16] which are found in many biologically active natural products. The work here would provide a useful method for their construction.

Experimental Section

All melting points are uncorrected. NMR spectra were measured using 270 MHz, 300 MHz and 500 MHz spectrometers with $CDCl_3$ as the solvent and $SiMe_4$ as the internal standard. Infrared (IR) absorption spectra were recorded as KBr pellets. All solvents were distilled and dried according to standard procedures.

Preparation of Epoxy Acylates

Acyclic tetrasubstituted epoxy acylates **1**, ***cis*-6a-c**, ***trans*-6a-c** and monocyclic *cis*-epoxy acylates ***cis*-13c**, ***cis*-20**, ***cis*-25** were prepared from the corresponding α,β-unsaturated ketones, synthesized by literature procedures,[17] 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) epoxidation of the allylic alcohol with *m*-CPBA in CH_2Cl_2, or with *t*-BuOOH and $VO(acac)_2$ in C_6H_6,[18] and iii) acylation of epoxy alcohol with acid chloride (or acid anhydride) in pyridine. Acyclic trisubstituted epoxy acylates ***cis*-10a-c** and ***trans*-10a-c** were prepared by epoxidation of commercially obtained nerol and geraniol followed by acylation. Monocyclic *trans*-epoxy acylates ***trans*-13a,c**, ***trans*-17b,c**, ***trans*-20**, ***trans*-25** and bicyclic *trans*-epoxy acylates ***trans*-30b,c** were prepared by epimerization of the *cis*-epoxy alcohol by the Mitsunobu reaction using benzoic acid, *p*-nitrobenzoic acid and (-)-camphanic acid.[19]

(2-Methyl-1-oxaspiro[2.5]oct-2-yl)methyl Benzoate (1): colorless oil; IR (KBr) 2932, 2859, 1725, 1451, 1314, 1275 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.47 (s, 3H), 1.54-1.79 (m, 10H), 4.35 (d, 1H, *J*= 11.5 Hz), 4.47 (d, 1H, *J*= 11.5 Hz), 7.41-7.57 (m, 3H), 8.05-8.11 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 16.0, 25.0, 25.1, 25.6, 30.7, 31.2, 62.6, 66.7, 67.3, 128.4, 129.6, 129.8, 133.1, 166.2. MS (EI) m/z (rel intensity) 260 (M^+, 0.02), 217 (0.1), 203 (0.2), 163 (0.1), 162 (0.7), 161 (0.3), 155 (0.1), 139 (0.2), 137 (0.2), 120 (2), 106 (10), 105 (100), 104 (15), 92 (2), 91 (2), 84 (2), 81 (6), 77 (14); HRMS (EI) Calcd for $C_{16}H_{20}O_3$ (M^+): 260.1412. Found: 260.1439.

***cis*-(3-Cyclohexyl-2,3-dimethyl-2-oxiranyl)methyl Benzoate (*cis*-6a):** colorless oil; IR (KBr) 1725, 1451, 1275 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.16-1.33 (m, 6H), 1.27 (s, 3H), 1.47 (s, 3H), 1.50-1.84 (m, 5H), 4.40 (ABq, 1H, *J*= 11.5 Hz), 4.50 (ABq, 1H, *J*= 11.5 Hz), 7.42-7.58 (m, 3H), 8.05-8.10 (m, 2H); Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.93; H, 8.56.

***cis*-(3-Cyclohexyl-2,3-dimethyl-2-oxiranyl)methyl *p*-Nitrobenzoate (*cis*-6b):** pale yellow oil; IR (KBr) 1728, 1609, 1530, 1451, 1348, 1277 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.17-1.84 (m, 11H), 1.29 (s, 3H), 1.49 (s, 3H), 4.46 (ABq, 1H, *J*= 11.9 Hz), 4.57 (ABq, 1H, *J*= 11.9 Hz), 8.23-8.35 (m, 4H); Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.69; H, 6.95; N, 4.09.

***cis*-(3-Cyclohexyl-2,3-dimethyl-2-oxiranyl)methyl Camphanoate (*cis*-6c):** (1:1 diastereomixture) colorless oil; IR (KBr) 1794, 1755, 1736, 1451, 1271 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.95, 0.97 (each s, total 3H), 1.05, 1.06 (each s, total 3H), 1.10 (s, 3H), 1.21 (s, 3H), 1.37 (s, 3H), 1.00-1.36 (m, 7H), 1.43-1.58 (m, 1H), 1.60-2.10 (m, 6H), 2.35-2.49 (m, 1H), 4.25-4.35 (m, 2H); HRMS (EI) Calcd for $C_{21}H_{32}O_5$ (M^+): 364.2250. Found: 364.2251.

***trans*-(3-Cyclohexyl-2,3-dimethyl-2-oxiranyl)methyl Benzoate (*trans*-6a):** colorless oil; IR (KBr) 1725, 1451, 1275 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.27 (s, 3H), 1,47 (s, 3H), 1.10-1.90 (m, 11H), 4.40 (ABq, 1H, *J*= 11.5 Hz), 4.51 (ABq, 1H, *J*= 11.5 Hz), 7.40-7.60 (m, 3H), 8.05-8.10 (m, 2H); Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.72; H, 8.41.

***trans*-(3-Cyclohexyl-2,3-dimethyl-2-oxiranyl)methyl *p*-Nitrobenzoate (*trans*-6b):** pale yellow crystals; mp 85-87 °C (*n*-hexane-ethyl acetate); IR (KBr) 2932, 2855, 1728, 1530, 1348, 1279, 1101 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.19-1.48 (m, 6H), 1.28 (s, 3H), 1.49 (s, 3H), 1.58 (m, 1H), 1.72-1.81 (m, 4H), 4.40 (ABq, 1H, *J*= 11.9 Hz), 4.48 (ABq, 1H, *J*= 11.9 Hz), 8.22 (d, 2H, *J*= 8.5 Hz), 8.31 (d, 2H, *J*= 8.5 Hz); Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.81; H, 6.83; N, 4.20.

***trans*-(3-Cyclohexyl-2,3-dimethyl-2-oxiranyl)methyl Camphanoate (*trans*-6c):** (1:1 diastereomixture) colorless oil; IR (KBr) 2932, 1792, 1755, 1750, 1740, 1451 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.96, 0.97 (each s, total 3H), 1.06 (s, 3H), 1.11 (s, 3H), 1.22, 1.23 (each s, total 3H), 1.00-1.39 (m, 7H), 1.40 (s, 3H), 1.41-1.60 (m, 1H), 1.62-2.10 (m, 6H), 2.34-2.50 (m, 1H), 4.19-4.35 (m, 2H); HRMS (EI) Calcd for $C_{21}H_{32}O_5$ (M^+): 364.2250. Found: 364.2247.

***cis*-[3-Methyl-3-(4-methyl-3-pentenyl)-2-oxiranyl]methyl Benzoate (*cis*-10a):** colorless oil; IR (KBr) 1732, 1530, 1350, 1277 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.38 (s, 3H), 1.42-1.80 (m, 2H), 1.62 (s, 3H), 1.70 (s, 3H), 2.14 (dt, 2H, *J*= 7.0, 7.0 Hz), 3.14 (dd, 1H, *J*= 4.0, 7.0 Hz), 4.27 (dd, 1H, *J*= 7.0, 12.0 Hz), 4.59 (dd, 1H, *J*= 4.0, 12.0 Hz), 5.05-5.20 (m, 1H), 7.39-7.62 (m, 3H), 8.04-8.13 (m, 2H); Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.52; H, 8.14.

***cis*-[3-Methyl-3-(4-methyl-3-pentenyl)-2-oxiranyl]methyl *p*-Nitrobenzoate (*cis*-10b):** pale yellow oil; IR (KBr) 2966, 2990, 1728, 1530, 1348, 1273 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.39 (s, 3H), 1.54-1.59 (m, 1H), 1.62 (s, 3H), 1.65-1.79 (m, 1H), 1.70 (s, 3H), 2.13-2.20 (m, 2H), 3.14 (dd, 1H, *J*= 3.5, 7.5 Hz), 4.28 (dd, 1H, *J*= 7.5, 12.0 Hz), 4.66 (dd, 1H, *J*= 3.5, 12.0 Hz), 5.05-5.20 (m, 1H), 8.23 (d, 2H, *J*= 9.0 Hz), 8.31 (d, 2H, *J*= 9.0 Hz); ^{13}C-NMR ($CDCl_3$) δ 17.6, 21.9, 24.1, 25.6, 33.2, 60.6, 60.9, 64.7, 122.9, 123.5, 130.8, 132.6, 135.0, 150.6, 164.5; Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39. Found: C, 63.85; H, 6.40; N, 4.58.

***cis*-[3-Methyl-3-(4-methyl-3-pentenyl)-2-oxiranyl]methyl Camphanoate (*cis*-10c):** (1:1 diastereomixture) colorless oil; IR (KBr) 1798, 1790, 1755, 1738, 1456, 1269 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.98, 0.99 (each s, total 3H), 1.08 (s, 3H), 1.13 (s, 3H), 1.35 (s, 3H), 1.45-1.73 (m, 3H), 1.62 (s, 3H), 1.70 (s, 3H), 1.90-1.98 (m, 1H), 2.01-2.15 (m, 3H), 2.42-2.50 (m, 1H), 3.03 (dd, 1H, *J*= 4.0, 7.0 Hz), 4.20, 4.22 (each dd, total 1H, *J*= 7.0, 12.0 Hz), 4.46 (dt, 1H, *J*= 12.0, 4.0 Hz), 5.09 (m, 1H); Anal. Calcd for $C_{20}H_{30}O_5$: C, 68.55; H, 8.63. Found: C, 68.76; H, 8.58.

***trans*-[3-Methyl-3-(4-methyl-3-pentenyl)-2-oxiranyl]methyl Benzoate (*trans*-10a):** colorless oil; IR (KBr) 2969, 2859, 1725, 1453, 1273 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.38 (s, 3H), 1.47-1.60 (m, 1H), 1.61 (s, 3H), 1.67 (s, 3H), 1.69-1.80 (m, 1H), 2.13 (dt, 2H, *J*= 7.5, 7.5 Hz), 3.14 (dd, 1H, *J*= 4.5, 7.0 Hz), 4.28 (dd, 1H, *J*= 7.0, 12.0 Hz), 4.58 (dd, 1H, *J*= 4.5, 12.0 Hz), 5.06-5.13 (m, 1H), 7.40-7.62 (m, 3H), 8.06-8.11 (m, 2H); Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.37; H, 8.18.

***trans*-[3-Methyl-3-(4-methyl-3-pentenyl)-2-oxiranyl]methyl *p*-Nitrobenzoate (*trans*-10b):** pale yellow oil; IR (KBr) 1730, 1529, 1273 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.39 (s, 3H), 1.47-1.79 (m, 2H), 1.62 (s, 3H), 1.67 (s, 3H), 2.12 (dt, 2H, *J*= 7.5, 7.5 Hz), 3.13 (dd, 1H, *J*= 4.0, 7.0 Hz), 4.32 (dd, 1H, *J*= 7.0, 12.0 Hz), 4.65 (dd, 1H, *J*= 4.0, 12.0 Hz), 5.06-5.13 (m, 1H), 8.25 (d, 2H, *J*= 8.5 Hz), 8.31 (d, 2H, *J*= 8.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 16.9, 17.7, 23.6, 25.7, 38.2, 59.5, 60.7, 64.9, 123.0, 123.6, 130.9, 132.4, 135.1, 150.7, 164.5; Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39. Found: C, 63.80; H, 6.66; N, 4.46.

***trans*-[3-Methyl-3-(4-methyl-3-pentenyl)-2-oxiranyl]methyl Camphanoate (*trans*-10c):** (1 : 1 diastereomixture) colorless oil; IR (KBr) 2969, 1792, 1755, 1738, 1269 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.98, 0.99 (each s, total 3H), 1.08 (s, 3H), 1.13 (s, 3H), 1.17-1.76 (m, 3H), 1.33, 1.34 (each s, total 3H), 1.58, 1.59 (each s, total 3H), 1.69, 1.70 (each s, total 3H), 1.88-2.12 (m, 4H), 2.40-2.50 (m, 1H), 3.03 (dd, 1H, *J*= 4.0, 7.0 Hz), 4.24 (dd, 1H, *J*= 7.0, 12.0 Hz), 4.44 (dt, 1H, *J*= 12.0, 4.0 Hz), 5.00-5.14 (m, 1H); Anal. Calcd for $C_{20}H_{30}O_5$: C, 68.55; H, 8.63. Found: C, 68.26; H, 8.41.

***cis*-5-Methyl-1-pentyl-6-oxabicyclo[3.1.0]hex-2-yl Camphanoate (*cis*-13c):** (1:1 diastereomixture) colorless oil; IR (KBr) 2957, 1794, 1752, 1381, 1171 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.89 (t, 3H, *J*= 7.0 Hz), 0.97, 0.99 (each s, total 3H), 1.08, 1.09 (each s, total 3H), 1.12 (s, 3H), 1.37 (s, 3H), 1.20-2.20 (m, 15H), 2.40-2.50 (m, 1H), 5.25-5.40 (m, 1H); Anal. Calcd for $C_{21}H_{32}O_5$: C, 69.20; H, 8.85. Found: C, 68.92; H, 8.79.

***trans*-5-Methyl-1-pentyl-6-oxabicyclo[3.1.0]hex-2-yl Benzoate (*trans*-13a):** colorless oil; IR (KBr) 2955, 2928, 2861, 1721, 1451, 1273, 1175 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.85 (t, 3H, *J*= 7.0 Hz), 1.28-1.61 (m, 8H), 1.47 (s, 3H), 1.86-1.98 (m, 4H), 5.54 (d, 1H, *J*= 5.0 Hz), 7.43-7.59 (m, 3H), 8.00-8.04 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 14.0, 15.5, 22.5, 25.0, 25.9, 27.5, 31.0, 32.2, 68.6, 70.0, 76.2, 128.3, 129.5, 130.2, 132.9, 165.5; HRMS (FAB) Calcd for $C_{18}H_{25}O_3$ (M^++H): 289.1803. Found: 289.1803.

***trans*-5-Methyl-1-pentyl-6-oxabicyclo[3.1.0]hex-2-yl *p*-Nitrobenzoate (*trans*-13b):** pale yellow crystals; mp 57-58 °C (*n*-hexane-ethyl acetate); IR (KBr) 2957, 2930, 1728, 1530, 1348, 1275 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.86 (t, 3H, *J*= 7.0 Hz), 1.26-1.50 (m, 7H), 1.49 (s, 3H), 1.60-1.76 (m, 1H), 1.80-2.05 (m, 4H), 5.58 (d, 1H, *J*= 5.0 Hz), 8.18 (d, 2H, *J*= 8.5 Hz), 8.31 (d, 2H, *J*= 8.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 14.0, 15.4, 22.5, 24.9, 25.8, 27.5, 30.8, 32.1, 68.6, 69.6, 77.4, 123.5, 130.5, 135.4, 150.5, 163.6; Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.79; H, 6.92; N, 4.20.

***trans*-5-Methyl-1-pentyl-6-oxabicyclo[3.1.0]hex-2-yl Camphanoate (*trans*-13c):** (1:1 diastereomixture) colorless oil; IR (KBr) 2957, 1794, 1754, 1732, 1312, 1266, 1169, 1103, 1063 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.86-0.91 (m, 3H), 0.96 (s, 3H), 1.06 (s, 3H), 1.26 (s, 3H), 1.26-2.05 (m, 15H), 1.42 (s, 3H), 2.35-2.50 (m, 1H), 5.41 (m, 1H); Anal. Calcd for $C_{21}H_{32}O_5$: C, 69.20; H, 8.85. Found: C, 68.91; H, 8.73.

***trans*-5-Methyl-6-oxabicyclo[3.1.0]hex-2-yl *p*-Nitrobenzoate (*trans*-17b):** pale yellow powder; mp 61-62 °C (*n*-hexane-ethyl acetate); IR (KBr) 1728, 1530, 1348, 1273 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.49 (s, 3H), 1.74-1.95 (m, 4H), 3.38 (s, 1H), 5.38 (d, 1H, *J*= 3.5 Hz), 8.12 (ABq, 2H, *J*= 9.0 Hz), 8.20 (ABq, 2H, *J*= 9.0 Hz); ^{13}C-

NMR ($CDCl_3$) δ 17.0, 28.0, 29.4, 62.0, 64.7, 76.6, 123.4, 130.6, 135.2, 150.4, 163.9; Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.29; H, 4.97; N, 5.21.

***trans*-5-Methyl-6-oxabicyclo[3.1.0]hex-2-yl Camphanoate (*trans*-17c):** (1:1 diastereomixture) colorless oil; IR (KBr) 2967, 1790, 1755, 1750, 1732, 1451, 1399 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.92 (s, 3H), 1.02 (s, 3H), 1.09 (s, 3H), 1.47, 1.49 (each s, total 3H), 1.58-2.05 (m, 7H), 2.32-2.45 (m, 1H), 3.27, 3.30 (each s, total 1H), 5.30 (d, 1H, *J*= 3.5 Hz); Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7. 53. Found: C, 65.06; H, 7.44.

***trans*-1-Butyl-6-methyl-7-oxabicyclo[4.1.0]hept-2-yl *p*-Nitrobenzoate (*trans*-20):** pale yellow powder; mp 71-72 °C (CH_2Cl_2-*n*-hexane); IR (KBr) 2872, 1728, 1609, 1539, 1410 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.76 (t, 3H, *J*= 7.0 Hz), 1.36 (s, 3H), 1.16-1.55 (m, 8H), 1.70-2.00 (m, 4H), 5.46 (t, 1H, *J*= 4.5 Hz), 8.20 (ABq, 2H, *J*= 8.5 Hz), 8.28 (ABq, 2H, *J*= 8.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 13.7, 15.6, 21.0, 22.9, 25.8, 26.4, 28.9, 29.9, 63.4, 64.1, 71.9, 123.5, 130.6, 135.5, 150.5, 163.7; Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.82; H, 6.94; N, 4.10.

***cis*-6-Methyl-7-oxabicyclo[4.1.0]hept-2-yl Camphanoate (*cis*-25):** (1:1 diastereomixture) colorless crystals; mp 58-59 °C (CH_2Cl_2-diethyl ether); IR (KBr) 2942, 1790, 1755, 1750, 1732, 1321 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.87, 0.89 (each s, total 3H), 0.94, 0.96 (each s, total 3H), 0.99, 1.00 (each s, total 3H), 1.22, 1.24 (each s, total 3H), 1.40-2.02 (m, 9H), 2.25-2.45 (m, 1H), 3.10-3.15 (m, 1H), 5.05-5.18 (m, 1H); Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.02; H, 7.64.

***trans*-6-Methyl-7-oxabicyclo[4.1.0]hept-2-yl Camphanoate (*trans*-25):** (1:1 diastereomixture) colorless oil; IR (KBr) 3567, 1798, 1790, 1732, 1456, 1397 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.95, 0.97 (each s, total 3H), 1.05, 1.06 (each s, total 3H), 1.11 (s, 3H), 1.34 (s, 3H), 1.20-1.55 (m, 3H), 1.60-1.79 (m, 2H), 1.85-2.10 (m, 4H), 2.35-2.52 (m, 1H), 2.90 (d, 1H, *J*= 12.5 Hz), 5.09-5.18 (m, 1H); Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 65,91; H, 7.65.

***trans*-10-Oxatricyclo[4.3.1.0^{1,6}]dec-7-yl *p*-Nitrobenzoate (*trans*-30b):** colorless crystals; mp 125-126 °C (*n*-hexane-ethyl acetate); IR (KBr) 2948, 1717, 1609, 1530, 1287 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.26-2.19 (m, 12H), 5.45 (d, 1H, *J* = 5.0 Hz), 8.16 (d, 2H, *J* = 9.0 Hz), 8.28 (d, 2H, *J* = 9.0 Hz); ^{13}C-NMR ($CDCl_3$) δ 20.2, 20.6, 22.4, 26.4, 28.2, 29.9, 65.8, 67.4, 78.1, 123.5, 130.6, 135.5, 150.5, 163.8; Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.22; H, 5.59; N, 4.66.

***trans*-10-Oxatricyclo[4.3.1.0^{1,6}]dec-7-yl Camphanoate (*trans*-30c):** (1:1 diastereomixture) colorless crystals; mp 91-92 °C (*n*-hexane-ethyl acetate); IR (KBr) 2934, 1790, 1737, 1315, 1173 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.97 (s, 3H), 1.07 (s, 3H), 1.13 (s, 3H), 1.40-2.60 (m, 16H), 5.26 (dd, 1H, *J* = 6.5, 9.0 Hz); Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 68.14; H, 7.70.

Lewis Acid Treatment of α,β-Epoxy Acylates : General Procedure

Reaction with BF3•Et2O. To a solution of epoxy acylate (0.1 mmol) in CH_2Cl_2 (2.8 ml) was added $BF_3•Et_2O$ (0.1 mmol) at 0°C under N_2, and the reaction mixture was stirred at 0°C for 10-30 min (TLC check). 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, and concentrated. The crude product was purified by column chromatography on silica gel (*n*-hexane-ethyl acetate) to give the pure rearrangement product.

Reaction with MABR. To a solution of MABR[4] (0.2 mmol) in CH_2Cl_2 (2.2 ml) was added an epoxy acylate (0.1 mmol) in CH_2Cl_2 (2.2 ml) at 0°C under Ar. The mixture was stirred at 0°C for 10-30 min (TLC check). After having been diluted with CH_2Cl_2, 1N HCl was added to the mixture. The same procedure as stated above gave the pure rearrangement product.

Reaction for Table 1

1 (45 mg, 0.173 mmol) and MABR (0.346 mmol) in dry CH_2Cl_2 (4 ml) gave **2** (2 mg, 4 %) and **3** (18 mg, 40 %).

2-(1-Methylcyclohexyl)-2-oxoethyl Benzoate (2): colorless oil; IR (KBr) 1732, 1721, 1277 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.23 (s, 3H), 1.35-1.60 (m, 8H), 1.99-2.05 (m, 2H), 5.12 (s, 2H), 7.41-7.58 (m, 3H), 8.08-8.13 (m, 2H) ; ^{13}C-NMR ($CDCl_3$) δ 22.7, 25.6, 30.9, 34.4, 47.1 (quaternary carbon), 65.2, 128.4, 129.5, 129.8, 133.2, 166.1, 207.4; HRMS (EI) Calcd for $C_{16}H_{20}O_3$ (M^+): 260.1412. Found: 260.1439.

(1-Acetylcyclohexyl)methyl Benzoate (3): colorless oil; IR (KBr) 1721, 1710, 1271 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.42-1.62 (m, 8H), 2.04-2.05 (m, 2H), 2.23 (s, 3H), 4.39 (s, 2H), 7.39-7.56 (m, 3H), 7.94-7.99 (m, 2H) ; ^{13}C-NMR ($CDCl_3$) δ 22.1, 25.5, 25.6, 30.1, 51.6, 68.9 (quaternary carbon), 128.3, 129.4, 129.5, 133.0, 165.9, 211.0.; HRMS (FAB) Calcd for $C_{16}H_{21}O_3$ (M^++H): 261.1491. Found: 261.1494.

Reactions for Table 2

entry	substrate		MABR	CH_2Cl_2	product	yield (%)
2	***cis*-6a**	53.7 mg (0.186 mmol)	0.373 mmol	4.5 ml	**7a** **8a**	58 (31.0 mg) 12 (6.5 mg)
3	***cis*-6b**	58.2 mg (0.175 mmol)	0.350 mmol	4.0 ml	**7b** **8b**	73 (42.7 mg) 6 (3.5 mg)
4	***cis*-6c**	27.9 mg (0.077 mmol)	0.153 mmol	1.8 ml	**7c** **8c**	82 (23.0 mg) 11 (3.1 mg)
6	***trans*-6a**	33.2 mg (0.115 mmol)	0.230 mmol	2.6 ml	**7a** **8a**	10 (3.2 mg) 52 (17.3 mg)
7	***trans*-6b**	32.0 mg (0.096 mmol)	0.192 mmol	3.0 ml	**7b** **8b**	23 (7.2 mg) 49(15.8 mg)
8	***trans*-6c**	156 mg (0.428 mmol)	0.855 mmol	9.4 ml	**7c** **8c**	74 (115.8 mg) 16 (24.4 mg)

3-Cyclohexyl-3-methyl-2-oxobutyl Benzoate (7a): colorless crystals; mp 71-72 °C (*n*-hexane-ethyl acetate); IR (KBr) 1732, 1721, 1451, 1368, 1277 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.02-1.48 (m, 5H), 1.15 (s, 6H), 1.58-1.85

(m, 6H), 5.10 (s, 2H), 7.42-7.60 (m, 3H), 8.08-8.11 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 20.9, 26.5, 26.8, 27.6, 45.1, 49.7 (quaternary carbon), 65.8, 128.4, 129.6, 129.9, 133.2, 166.1, 208.0; Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.60; H, 8.23.

3-Cyclohexyl-3-methyl-2-oxobutyl *p*-Nitrobenzoate (7b): pale yellow crystals; mp 99-100 °C (*n*-hexane-ethyl acetate); IR (KBr) 2932, 2857, 1736, 1721, 1530, 1418, 1348, 1279 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.00-1.80 (m, 11H), 1.16 (s, 6H), 5.15 (s, 2H), 8.20-8.30 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 20.9, 26.4, 26.8, 27.5, 45.1, 49.7 (quaternary carbon), 66.5, 123.5, 131.0, 135.0, 150.7, 164.2, 207.5; Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.59; H, 6.90; N, 4.10.

3-Cyclohexyl-3-methyl-2-oxobutyl Camphanoate (7c): pale yellow crystals; mp 114-115 °C (*n*-hexane-ethyl acetate); IR (KBr) 2855, 1763, 1748, 1721, 1449, 1264 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.06, 1.07, 1.09 (each s, total 15H), 0.82-2.10 (m, 14H), 2.39-2.52 (m, 1H), 4.89 (ABq, 1H, *J*= 16.5 Hz), 4.99 (ABq, 1H, *J*= 16.5 Hz); HRMS (FAB) Calcd for $C_{21}H_{33}O_5$ (M^++H): 365.2328. Found: 365.2314.

2-Cyclohexyl-2-methyl-3-oxobutyl Benzoate (8a): colorless crytals; mp 63.5-64.5 °C (*n*-hexane-ethyl acetate); IR (KBr) 2930, 2855, 1723, 1451, 1269 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.06-1.85 (m, 11H), 1.20 (s, 3H), 2.19 (s, 3H), 4.38 (d, 1H, *J*= 9.0 Hz), 4.48 (d, 1H, *J*= 9.0 Hz), 7.40-7.59 (m, 3H), 7.94-7.97 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 15.5, 26.7, 26.8, 27.2, 27.3, 28.1, 28.3, 43.2, 55.1 (quaternary carbon), 69.9, 128.9, 130.0, 130.3, 133.6, 166.8, 211.7; Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 75.06; H, 8.45.

2-Cyclohexyl-2-methyl-3-oxobutyl *p*-Nitrobenzoate (8b): pale yellow crystals; mp 109-110 °C (*n*-hexane-ethyl acetate); IR (KBr) 2930, 2857, 1728, 1709 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.10-1.79 (m, 11H), 1.23 (s, 3H), 2.20 (s, 3H), 4.40 (d, 1H, *J*= 11.0 Hz), 4.56 (d, 1H, *J*= 11.0 Hz), 8.11 (d, 2H, *J*= 9.0 Hz), 8.27 (d, 2H, *J*= 9.0 Hz); ^{13}C-NMR (C_6D_6) δ 15.2, 25.6, 26.5, 26.9, 27.0, 27.7, 27.9, 42.7, 54.5 (quaternary carbon), 70.0, 123.6, 130.4, 134.9, 150.7, 164.3, 208.8; Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.96; H, 6.85; N, 4.18.

2-Cyclohexyl-2-methyl-3-oxobutyl Camphanoate (8c): pale yellow crystals; mp 81-83 °C (*n*-hexane-ethyl acetate); IR (KBr) 2930, 1792, 1755, 1736, 1707, 1266 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.90, 0.91 (each s, total 3H), 0.98, 0.99 (each s, total 3H), 1.07 (s, 3H), 1.14, 1.16 (each s, total 3H), 0.90-1.25 (m, 6H), 1.38-2.05 (m, 8H), 2.12, 2.13 (each s, total 3H), 2.25-2.40 (m, 1H), 4.15 (dd, 1H, *J*= 11.0, 14.0 Hz), 4.41 (dd, 1H, *J*= 6.5, 11.0 Hz); HRMS (FAB) Calcd for $C_{21}H_{33}O_5$ (M^++H): 365.2328. Found: 365.2343.

Reactions for Scheme 1

entry	substrate	MABR	CH_2Cl_2	product yield (%)
1	***cis*-10a** 37.3 mg (0.136 mmol)	0.272 mmol	3.1 ml	**11a** 70 (26.1 mg)
2	***cis*-10b** 44.6 mg (0.140 mmol)	0.280 mmol	3.2 ml	**11b** 83 (36.8 mg)
3	***cis*-10c** 100 mg (0.285 mmol)	0.568 mmol	6.3 ml	**11c** 91 (91.3 mg)
5	***trans*-10a** 34.0 mg (0.124 mmol)	0.248 mmol	2.8 ml	**11a** 48 (16.4 mg)
6	***trans*-10b** 73.4 mg (0.230 mmol)	0.460 mmol	4.9 ml	**11b** 76 (55.5 mg)
7	***trans*-10c** 96.0 mg (0.274 mmol)	0.549 mmol	6.0 ml	**11c** 81 (78.1 mg)

3,7-Dimethyl-2-oxo-6-octenyl Benzoate (11a): pale yellow oil; IR (KBr) 2969, 1725, 1453, 1277 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.17 (d, 3H, *J*= 7.0 Hz), 1.37-1.58 (m, 1H), 1.60 (s, 3H), 1.67 (s, 3H), 1.75-1.86 (m, 1H), 2.01 (m, 2H), 2.68 (tq, 1H, *J*= 7.0, 7.0 Hz), 4.92 (ABq, 1H, *J*= 17.0 Hz), 4.96 (ABq, 1H, *J*= 17.0 Hz), 5.03-5.10 (m, 1H), 7.41-7.60 (m, 3H), 8.11-8.12 (m, 2H); Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.45; H, 8.19.

3,7-Dimethyl-2-oxo-6-octenyl *p*-Nitrobenzoate (11b): colorless crystals; mp 65-66 °C (*n*-hexane-ethyl acetate); IR (KBr) 2969, 2930, 1736, 1723, 1530, 1414, 1352, 1273 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.18 (d, 3H, *J*= 7.0 Hz), 1.40-1.59 (m, 1H), 1.62 (s, 3H), 1.69 (s, 3H), 1.75-1.86 (m, 1H), 2.10 (dt, 2H, *J*= 7.5, 7.5 Hz), 2.67 (tq, 1H, *J*= 7.0, 7.0 Hz), 4.98 (ABq, 1H, *J*= 16.5 Hz), 5.03 (ABq, 1H, *J*= 16.5 Hz), 5.04-5.11 (m, 1H), 8.25 (d, 2H, *J*= 9.0 Hz), 8.32 (d, 2H, *J*= 9.0 Hz); ^{13}C-NMR ($CDCl_3$) δ 16.2, 17.7, 25.5, 25.7, 32.7, 42.2, 68.0, 123.3, 123.6, 131.0, 132.7, 134.7, 150.7, 164.0, 206.2; Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39. Found: C, 63.90; H, 6.52; N, 4.38.

3,7-Dimethyl-2-oxo-6-octenyl Camphanoate (11c): colorless oil; IR (KBr) 2971, 1796, 1790, 1761, 1732, 1377, 1312 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.11 (d, 3H, *J*= 7.0 Hz), 1.13, 1.15 (each s, total 9H), 1.30-1.50 (m, 1H), 1.59 (s, 3H), 1.68 (s, 3H), 1.65-2.15 (m, 6H), 2.49 (ddd, 1H, *J*= 4.0, 11.0, 13.5 Hz), 2.59 (tq, 1H, *J*= 7.0, 7.0 Hz), 4.75-4.96 (m, 2H), 5.00-5.10 (m, 1H); Anal. Calcd for $C_{20}H_{30}O_5$: C, 68.55; H, 8.63. Found: C, 68.48; H, 8.38.

Reactions for Table 3

entry	substrate	Lewis acid	CH_2Cl_2	product yield
3	***cis*-13c** 20.1 mg (0.053 mmol)	$BF_3{\cdot}Et_2O$ 0.006 ml (0.053 mmol)	1.0 ml	**14c** 12.6 mg (63 %)
6	***trans*-13c** 19.2 mg (0.050 mmol)	$BF_3{\cdot}Et_2O$ 0.006 ml (0.050 mmol)	1.0 ml	**15c** 10.7 mg (56 %)
7	***trans*-13c** 20.0 mg (0.055 mmol)	MABR (0.105 mmol)	2.0 ml	**15c** 16.5 mg (83 %)

***(1RS, 3RS)*-3-Methyl-2-oxo-3-pentylcyclopentyl Camphanoate (14c):** colorless oil; IR (KBr) 1794, 1755, 1752, 1264 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.87 (t, 3H, *J*= 7.0 Hz), 1.05 (s, 3H), 1.08 (s, 3H), 1.09 (s, 3H), 1.12 (s, 3H), 1.15-1.50 (m, 8H), 1.60-1.78 (m, 1H), 1.80-2.18 (m, 5H), 2.30-2.59 (m, 2H), 5.28-5.33 (m, 1H); Anal. Calcd for $C_{21}H_{32}O_5$: C, 69.20; H, 8.85. Found: C, 69.06; H, 8.77.

***(1RS, 3SR)*-3-Methyl-2-oxo-3-pentylcyclopentyl Camphanoate (15c):** colorless oil; IR (KBr) 1796, 1757, 1750, 1738 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.86-0.89 (m, 3H), 1.03-1.13 (m, 12H), 1.10-2.10 (m, 14H), 2.20-2.50 (m, 2H), 5.28-5.37 (m, 1H); Anal. Calcd for $C_{21}H_{32}O_5$: C, 69.20; H, 8.85. Found: C, 68.80; H, 8.55.

Reactions for Table 4

entry	substrate	Lewis acid	CH_2Cl_2	product yield
3	***trans*-17b** 100 mg (0.38 mmol)	$BF_3{\cdot}Et_2O$ 0.047 ml (0.38 mmol)	3.8 ml	**19b** 21.6 mg (22 %)
5	***trans*-17c** 101 mg (0.343 mmol)	$BF_3{\cdot}Et_2O$ 0.042 ml (0.343 mmol)	3.4 ml	**19c** 47.9 mg (47 %)
6	***trans*-17c** 101 mg (0.343 mmol)	MABR (0.686 mmol)	3.4 ml	**19c** 8.3 mg (8 %)

***(1RS, 3RS)*-3-Methyl-2-oxocyclopentyl *p*-Nitrobenzoate (19b):** pale yellow oil; IR (KBr) 1755, 1728, 1532, 1348 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.20 (d, 3H, *J*= 6.5 Hz), 1.35-1.62 (m, 1H), 1.85-2.62 (m, 4H), 5.28 (dd, 1H, *J*= 8.0, 11.5 Hz), 8.22 (ABq, 2H, *J*= 9.0 Hz), 8.29 (ABq, 2H, *J*= 9.0 Hz); ^{13}C-NMR ($CDCl_3$) δ 14.9, 26.3, 27.3, 41.8, 77.2, 123.5, 130.9, 134.7, 150.6, 163.8, 213.4; HRMS (EI) Calcd for $C_{13}H_{13}NO_5$ (M^+): 263.0793. Found: 263.0817.

***(1RS, 3RS)*-3-Methyl-2-oxocyclopentyl Camphanoate (19c):** colorless oil; IR (KBr) 2878, 1790, 1771, 1748, 1732, 1456, 1264 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.98, 0.99 (each s, total 3H), 1.03 (s, 3H), 1.07 (s, 3H), 1.11, 1.13 (each s, total 3H), 1.15-2.52 (m, 9H), 5.10-5.36 (m, 1H); HRMS (EI) Calcd for $C_{16}H_{22}O_5$ (M^+): 294.1467. Found: 294.1462.

Reactions for Scheme 2

entry	amount of *trans*-20	Lewis acid	CH_2Cl_2	product yield
3	206.6 mg (0.62 mmol)	$BF_3{\cdot}Et_2O$ 0.077 ml (0.62 mmol)	6.2 ml	**23** 159 mg (77 %) **24** 16.5 mg (8 %)
4	100 mg (0.30 mmol)	MABR (0.60 mmol)	3.0 ml	**24** 80.0 mg (80 %)

***(1RS, 3SR)*-3-Butyl-3-methyl-2-oxocyclohexyl *p*-Nitrobenzoate (23):** colorless oil; IR (KBr) 2872, 1738, 1717, 1350 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.90 (t, 3H, *J*= 7.0 Hz), 1.30 (s, 3H), 1.15-1.40 (m, 4H), 1.45-2.10 (m, 7H), 2.35-2.47 (m, 1H), 5.70 (dd, 1H, *J*= 6.0, 12.5 Hz), 8.24 (ABq, 2H, *J*= 9.0 Hz), 8.28 (ABq, 2H, *J*= 9.0 Hz); ^{13}C-NMR ($CDCl_3$) δ 14.1, 19.6, 22.4, 23.5, 25.9, 33.1, 37.7, 38.0, 48.7, 75.4, 123.4, 130.8, 135.2, 150.4, 163.7, 207.4; HRMS (FAB) Calcd for $C_{18}H_{24}NO_5$ (M^++H): 334.1655. Found: 334.1649.

***(1RS, 2RS)*-2-Methyl-2-pentanoylcyclopentyl *p*-Nitrobenzoate (24):** pale yellow crystals; mp 108-109 °C (CH_2Cl_2-*n*-hexane); IR (KBr) 2961, 1725, 1713, 1532, 1348 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, 3H, *J*= 7.0 Hz), 0.83-1.03 (m, 1H), 1.22-1.91 (m, 9H), 2.08 (s, 3H), 2.00-2.45 (m, 2H), 5.37 (d, 1H, *J*= 5.0 Hz), 8.05 (ABq, 2H, *J*= 9.0 Hz), 8.24 (ABq, 2H, *J*= 9.0 Hz); ^{13}C-NMR ($CDCl_3$) δ 13.9, 21.1, 23.2, 26.6, 27.1, 28.3, 31.6, 34.3, 64.1, 84.1, 123.5, 130.5, 135.2, 150.5, 163.6, 208.3; Anal. Calcd for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.76; H, 6.94; N, 4.12.

Reactions for Scheme 3

entry	substrate	Lewis acid	CH_2Cl_2	product yield
1	***cis*-25** 131.5 mg (0.426 mmol)	$BF_3{\cdot}Et_2O$ 0.053 ml (0.426 mmol)	4.3 ml	**26** 63.9 mg (49 %)
2	***cis*-25** 122.0 mg (0.396 mmol)	MABR (0.791 mmol)	8.7 ml	**27** 81.9 mg (67 %)
3	***trans*-25** 184.0 mg (0.597 mmol)	$BF_3{\cdot}Et_2O$ 0.074 ml (0.597 mmol)	6.0 ml	**28** 114.4 mg (62 %)
4	***trans*-25** 124.7 mg (0.404 mmol)	MABR (0.809 mmol)	8.9 ml	**29** 42.4 mg (34 %)

***(1RS, 3SR)*-3-Methyl-2-oxocyclohexyl Camphanoate (26):** colorless needles; mp 115-116 °C (*n*-hexane-CH_2Cl_2); IR (KBr) 2973, 1784, 1750, 1730, 1719, 1399 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.04 (d, 3H, *J*= 6.5 Hz), 1.05 (s, 3H), 1.10 (s, 3H), 1.11, 1.13 (each s, total 3H), 1.20-2.60 (m, 11H), 5.19, 5.24 (each dd, total 1H, *J*= 6.5, 11.5 Hz); Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.11; H, 7.58.

***(1RS, 2SR)*-2-Formyl-2-methylcyclopentyl Camphanoate (27):** colorless crystals; mp 64-66 °C (*n*-hexane-ethyl acetate); IR (KBr) 2973, 1790, 1754, 1748, 1732, 1727, 1105 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.93, 0.94 (each s, total 3H), 1.02 (s, 3H), 1.11 (s, 3H), 1.19 (s, 3H), 1.40-2.45 (m, 10H), 5.17 (m, 1H), 9.67, 9.69 (each s, total 1H); HRMS (FAB) Calcd for $C_{17}H_{25}O_5$ (M^++H): 309.1702. Found: 309.1679.

***(1RS, 3RS)*-3-Methyl-2-oxocyclohexyl Camphanoate (28):** colorless crystals; mp 110-112 °C (*n*-hexane-ethyl acetate); IR (KBr) 1790, 1759, 1727, 1266 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.01 (s, 3H), 1.04 (s, 3H), 1.09, 1.10 (each s, total 3H), 1.17 (d, 3H, *J*= 7.0 Hz), 1.60-2.19 (m, 9H), 2.36-2.50 (m, 1H), 2.70-2.81 (m, 1H), 5.32 (m, 1H); Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.09; H, 7.79.

***(1RS, 2RS)*-2-Formyl-2-methylcyclopentyl Camphanoate (29):** colorless oil; IR (KBr) 2973, 1790, 1755, 1748, 1738, 1732, 1397, 1314, 1271 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.96 (s, 3H), 1.05, 1.06 (each s, total 3H), 1.12 (s, 3H), 1.15, 1.16 (each s, total 3H), 1.50-2.50 (m, 10H), 5.41 (m, 1H), 9.50, 9.51 (each s, total 1H); HRMS (EI) Calcd for $C_{17}H_{24}O_5$ (M^+): 308.1624. Found: 308.1631.

Reactions for Table 5

entry	substrate	Lewis acid	CH_2Cl_2	product yield
2	***trans*-30b** 100 mg (0.33 mmol)	BF_3·Et_2O 0.041 ml (0.33 mmol)	3.3 ml	**31b** 63.0 mg (63 %)
3	***trans*-30c** 95.4 mg (0.285 mmol)	BF_3·Et_2O 0.035 ml (0.285 mmol)	2.9 ml	**31c** 62.0 mg (65 %)
4	***trans*-30b** 50.0 mg (0.165 mmol)	MABR (0.33 mmol)	4.0 ml	**31b** 12.0 mg (24 %)

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