Table II. ^{13}C and ^{1}H Assignments and FLOCK Correlations for 35a

position	^{13}C	$^{1}H^{a}$	C–H corr
1	124.08	7.89d	3
2	134.71	7.42t	4
3	128.02	7.65t	1
4	120.01	7.89d	
5	149.98		3, 11
6	134.02		2, 4
7	187.2		
8	135.48		11
9	130.59		10
10	135.48	7.74s	17
11	125.31	7.31s	13
12	136.35		14
13	129.43	7.00c	11, 13
14	127.15	6.80c	14
15	127.5	6.91t	13
16	135.28		18
17	130.49	7.08d	10, 17, 19
18	127.04	6.83c	18
19	128.43	7.00c	17

[a] c = centered at, d = doublet, t = triplet.

Thermolysis of 31. A solution of acetylenic alcohol 31 (169 mg, 0.55 mmol) in 20 mL of decalin was refluxed for 2 h, at which time the reaction was judged to be complete by TLC. The mixture was washed with hexanes (400 mL) over a plug of silica (20 g) and then eluted with ether (100 mL), CH_2Cl_2 (100 mL), and EtOAc (100 mL). The combined eluents were chromatographed on a Chromatotron plate (2 mm, 3:1 hexanes/CH_2Cl_2 → pure CH_2Cl_2). The following fractions were obtained:

(*E*,*Z*)-2,3-Dibenzylidene-1-indanone (35a) (18.6 mg, 11%): ^{1}H and ^{13}C NMR (see Table II); IR (CH_2Cl_2) 1703, 1615 cm^{-1}; MS (*m*/*e*) 308 (M^+, 100), 307 (43), 306 (33), 231 (54), 202 (38), 138 (23); HRMS calcd for $C_{23}H_{16}O$ 308.1201, found 308.1210.

4-Benzylidene-3-phenyl-1,4-naphthoquinonemethides (36) (38.9 mg, 23%) (isolated as 3:1 *Z*/*E* mixture): ^{1}H NMR δ *Z* (major) 8.20 (1 H, d, *J* = 8.4 Hz), 7.63 (1 H, d, *J* = 8.6 Hz), 7.43 (1 H, t, *J* = 7.9 Hz), 7.15 (1 H, s, br), 6.53 (1 H, d, *J* = 0.5 Hz); *E* (minor) 8.25 (1 H, d, *J* = 7.8 Hz), 8.10 (1 H, d, *J* = 7.5 Hz), 7.95 (1 H, d, *J* = 1.5 Hz), 7.67 (1 H, t, *J* = 7.2 Hz), 6.70 (1 H, d, *J* = 1.5 Hz); (overlapping peaks) 7.56–7.46 (m), 7.3–7.2 (m), 7.03–6.92 (m); ^{13}C-NMR δ *Z* (major) 184.98, 156.95, 141.69, 138.45, 136.82, 135.34, 132.93, 132.52, 130.23, 129.36, 129.21, 129.01, 128.79, 128.73, 128.62, 128.53, 128.49, 126.18, 126.10; *E* (minor) 185.25, 152.99, 139.97, 139.22, 138.58, 135.82, 132.04, 130.75, 129.87, 128.32, 127.86, 127.77, 127.73, 127.41, 126.30, 122.71; IR (CH_2Cl_2) 1641, 1600 cm^{-1}; MS (*m*/*e*, int) 308 (M^+, 77), 230 (100), 202 (50), 100 (89); HRMS calcd for $C_{23}H_{16}O$ 308.1201, found 308.1162.

10-Phenylbenzo[*b*]fluorenone (37) (25.4 mg, 15%): mp 218–219 °C (lit.[13] mp 219 °C); ^{1}H NMR δ 7.31 (td, *J* = 7.4, 0.95 Hz), 7.4–7.35 (3 H, m), 7.65–7.49 (7 H, m), 7.75 (1 H, dt, *J* = 7.5, 0.8 Hz), 7.86 (1 H, dt, *J* = 8.1, 0.6 Hz), 7.92 (1 H, s); ^{13}C NMR d 118.67, 120.64, 124.13, 126.76, 127.95, 128.03, 128.62, 128.70, 128.96, 129.15, 129.52, 133.77, 134.64, 135.44, 136.27, 136.60, 138.36, 141.18, 144.0, 192.2; IR (CH_2Cl_2) 1711 cm^{-1}; MS (*m*/*e*, int) 306 (M^+, 100), 305 (77), 276 (38), 138 (39); HRMS calcd for $C_{23}H_{14}O$ 306.1044, found 306.1023.

Acknowledgment. The financial support of NSERC (Canada) is gratefully acknowledged.

Supplementary Material Available: ^{1}H or ^{13}C NMR spectra of **15**, **23**, **26**, **29**, **31**, **35a**, **36**, and **37** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Molecular Sieve Controlled Diastereoselectivity: Effect in the Palladium-Catalyzed Cyclization of *cis*-1,2-Divinylcyclohexane with α-Oxygen-Substituted Acids as Chiral Nucleophiles

Louise Tottie, Peter Baeckström, and Christina Moberg*

Department of Organic Chemistry, Royal Institute of Technology, S-10044 Stockholm, Sweden

Jörgen Tegenfeldt

Department of Inorganic Chemistry, Uppsala University, S-75121 Uppsala, Sweden

Andreas Heumann*

Université d'Aix-Marseille, Faculté de St. Jérôme, URA 1410, ENSSPICAM, F-13013 Marseille, France

Received January 27, 1992

Molecular sieves have been shown to improve greatly the stereoselectivity in the palladium(II)-catalyzed reaction of *cis*-1,2-divinylcyclohexane with chiral acids. Reactions run with molecular sieves and derivatives of (*R*)-lactic acids as nucleophiles always yielded products with *S* configuration at the newly formed chiral center in contrast to reactions without molecular sieves that gave products with either *S* or *R* configuration at this chiral center. It appears that this effect has not been observed previously. Only water-containing molecular sieves increased the stereoselectivity. A chiral palladium complex was formed faster in the presence of molecular sieves, but use of this complex as catalyst in the cyclization did not result in increased selectivity. The best stereoselectivity was found for molecular sieves with a high sodium content (Lancaster 13X and 4-Å sieves).

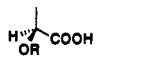
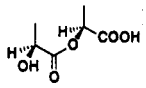
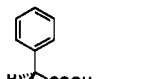
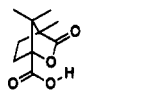
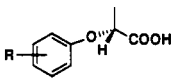
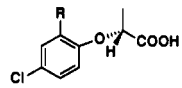
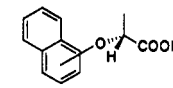
Molecular sieves have recently been shown to greatly improve the stereoselectivity in some titanium-catalyzed reactions such as the Sharpless epoxidation,[1] a Diels–Alder cyclization,[2] a glyoxylate–ene reaction,[3] and the aluminum-catalyzed ene reaction of prochiral aldehydes with alkenes.[4]

(1) (a) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922. (b) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

(2) (a) Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* **1986**, 1967. (b) Narasaka, K.; Inoue, M.; Yamada, T.; Sugimori, J.; Iwasawa, N. *Chem. Lett.* **1987**, 2409. (c) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340. (d) Narasaka, K.; Tanaka, H.; Kanai, F. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 387.

0022-3263/92/1957-6579$03.00/0

Table I. Reactions Run without Molecular Sieves

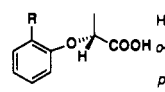
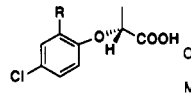
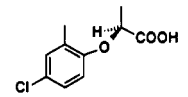
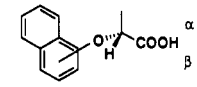
entry	R*COOH structure	R	no.	config at C7 of major diast.[a]	yield,[b] %	product	de,[c] %
1		H	3	R	48-72[d]	20[e]	6-7[e]
2		Ac	4	R	51	21	9
3		*i*PrCO	5	S	46	22	16
4			6	R	48-72[d]	23	18
5		H	7	S	21	24	8
6		Ac	8	S	45	25	22
7		Me	9	S	31	26	11
8			10	S	43	27	19[f]
9		H	11	R	40	28	12.5
10		*o*-F	12	-	33	29	0[e]
11		*p*-F	13	R	32	30	4
12		*o*-Ph	14	R	32	31	14
13		Cl	15	S	65	32	17
14		Me	16	R	31	33	17
15		α	18	R	22	35	1.4
16		β	19	R	32	36	26

[a] Determined according to ref 10. [b] Yield after chromatography. [c] Determined by GC on SE-30-type columns. [d] **20** and **23** in a mixture (62:38 by GC). [e] Determined by ^{1}H NMR. [f] According to $[\alpha]_D$.

In the Sharpless epoxidation, it was first shown that the presence of catalytic amounts of metal hydrides and silica gel greatly increase the reaction rate.[5] The subsequent finding of the beneficial effect of 3- or 4-Å molecular sieves, under catalytic reaction conditions, was attributed to the water-scavenging properties of the sieves.[1b] In the titanium-catalyzed Diels–Alder and glyoxylate–ene reactions, the same chiral catalyst was employed. In the glyoxylate–ene reaction, it was shown that the role of the molecular sieves was to form the chiral catalyst more efficiently.[3b]

During our studies of the oxidative cyclization of *cis*-1,2-divinylcyclohexane catalyzed by $Pd(OAc)_2$/*p*-benzoquinone/MnO_2 using chiral carboxylic acids as nucleophiles, we found, quite unexpectedly, that the addition of molecular sieve powders resulted not only in a markedly enhanced selectivity but also, in some cases, in reversal of the diastereofacial selectivity.[6] To our knowledge, this is the first time such an effect has been observed in palladium-promoted synthesis. In this paper, we present results from further investigations of this reaction aimed at elucidating the effect of the structure of the nucleophile on the diastereoselectivity and the origin of the favorable influence of the molecular sieves.

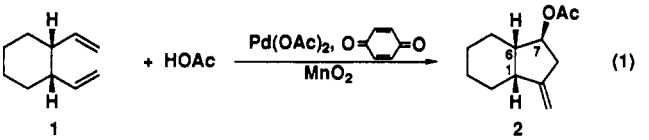
Table II. Reactions Run with Molecular Sieves 13X[a]

entry	R*COOH structure	R	no.	config at C7 of major diast[b]	yield,[c] %	product	de,[d] %
1		H	11	S	28	28	43
2		*o*-F	12	S	36	29	54[e]
3		*p*-F	13	S	24	30	51
4		*o*-Ph	14	S	41	31	43
5		Cl	15	S	39	32	62
6		Me	16	S	39	33	18
7			17	R	39	34	14
8		α	18	S	28	35	43
9		β	19	S	28	36	36

[a] One g of Lancaster 13X/mmol of diene 1. [b] Determined according to ref 10. [c] Yield after chromatography. [d] Determined by GC on SE-30-type columns. [e] Determined by ^{19}F NMR.

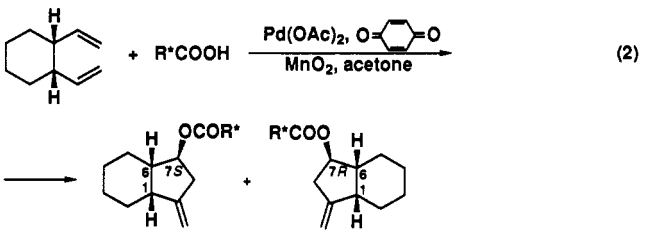
Results

Reaction of *cis*-1,2-divinylcyclohexane (1) in acetic acid in the presence of $Pd(OAc)_2$/*p*-benzoquinone/MnO_2 (1/4/22, 1–5 mol % Pd) yields a racemic mixture of (1*R**,6*S**,7*S**)-7-acetoxy-9-methylenebicyclo[4.3.0]nonane (2) in high yield without formation of regio- and diastereoisomers (eq 1).[7]



1 2 (1)

When the acetic acid was replaced by an organic solvent and monochiral acids such as mandelic and lactic acid derivatives were used as nucleophiles, moderate but significant inductions were observed (eq 2, Table I).[8] Among



(2)

the mandelic acid derivatives tried, the chiral discrimination of the enantiotopic double bonds of the diene 1 was found to be best for the acetylated acid. Particularly noteworthy were the reactions run with derivatives of lactic acid (Table I, entries 9–16), which were easily prepared by the Mitsunobu reaction of the substituted phenol with methyl or ethyl lactate followed by alkaline hydrolysis,[9] since it was found that the nature and position of the substituents on the phenyl ring considerably influenced

(3) (a) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1989**, *111*, 1940. (b) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 3949.

(4) Maruoka, K.; Hoshino, Y.; Shirasaka, T.; Yamamoto, H. *Tetrahedron Lett.* **1988**, *29*, 3967.

(5) (a) Wang, Z. M.; Zhou, W. S.; Lin, G. Q. *Tetrahedron Lett.* **1985**, *26*, 6221. (b) Wang, Z. M.; Zhou, W. S. *Tetrahedron* **1987**, *43*, 2935.

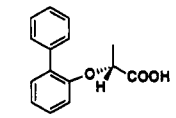
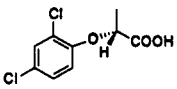
(6) Heumann, A.; Tottie, L.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1991**, 218.

(7) Antonsson, T.; Moberg, C.; Tottie, L.; Heumann, A. *J. Org. Chem.* **1989**, *54*, 4914.

(8) Heumann, A.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1988**, 1516.

(9) (a) Mitsunobu, O. *Synthesis* **1981**, 1. (b) Varasi, M.; Walker, K. A. M.; Maddox, M. L. *J. Org. Chem.* **1987**, *52*, 4235. (c) Castro, B. In *Organic Reactions*; Wiley: New York, 1983; Vol. 29, 1–162. (d) It has been shown that the enantiomeric purity isn't lost during the alkaline hydrolysis: Burkard, U.; Effenberger, F. *Chem. Ber.* **1986**, *119*, 1594.

Table III. Reactions Run with Different Amounts of 13X[a]

entry	R*COOH structure	no.	amt, g	config at C7 of major diast[b]	yield,[c] %	product	de,[d] %
1		14	-	R	32	31	14
2			0.5	S	34		34
3			1	S	41		43
4			2	S	32		56
5		15	-	S	65	32	17
6			1	S	39		62
7			3	S	27		76

[a] Standard conditions with 1 mmol of diene 1 in all experiments. [b] Determined according to ref 10. [c] Yield after chromatography. [d] Determined by GC on SE-30-type columns.

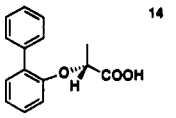
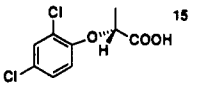
the stereochemical outcome of the reaction. Compared to the *O*-phenyllactic acid **11**, which lacks substituents on the phenyl ring (entry 9), acids with substituents on the phenyl ring could both decrease (entries 10, 11, and 15) and increase the selectivity (entries 13, 14, and 16). No straightforward relationship between the substitution pattern and the stereochemical outcome of the reaction was found, however. A dramatic difference in selectivity was observed for the differently substituted acids **18** and **19** (entries 15 and 16). The acid **19** gave a significant de (26%), whereas the acid **18** gave no selectivity at all.

Effect of Molecular Sieves. The addition of molecular sieves Lancaster 13X (powder) to an otherwise identical reaction mixture improved the stereoselectivity dramatically (Table II).[6] The most spectacular increase in selectivity was observed for (*R*)-2-(2-fluorophenoxy)propionic acid (**12**), where the diastereomeric excess was raised from 0 to 54% (Table II), and for (*R*)-2-(2,4-dichlorophenoxy)propionic acid (**15**), where the selectivity was improved from 17 to 76% de (Table III). The same effect was observed when the sieves were recovered and reused. Another interesting observation was the fact that when acids with *R* configuration were used the presence of molecular sieves always resulted in *S* configuration at C7 of the major diastereomer (eq 2), in contrast to reactions without molecular sieves which yielded products with either *S* or *R* configuration at this chiral center (Table I).[10] Thus, addition of molecular sieves caused reversal of the diastereofacial selectivity for the nucleophiles **11**, **13**, **14**, **16**, and **19**.

When mandelic acid **7** was used in the cyclization in the presence of Lancaster 13X, the result was a low yield of the expected product contaminated by an impurity. Moreover, product remained on the sieves even after the usual Soxhlet extraction (IR evidence). Similarly, use of acetylated mandelic acid **8** together with Lancaster 13X yielded a product contaminated by an impurity that could not be removed by chromatography. This impurity made it impossible to measure the diastereomeric excess by NMR. No product remained on the sieves in the latter case.

Reaction Conditions. As a consequence of lower nucleophile concentration (*c* 0.77 M) and lower nucleophilicity compared to the solvolytic conditions used previously, yields became poorer and the reaction times increased

Table IV. Reactions Run with Different Kinds of Molecular Sieves[a]

entry	R*COOH structure	no.	mol siev	config at C7 of major diast[b]	yield,[c] %	product	de,[d] %
1		14	-	R	32	31	14
2			3Å	S	18		13
3			4Å	S	26		58
4			13X	S	41		56
5			NaY	S	47		7
6			USY	R	54		13
7		15	-	S	65	32	17
8			3Å	S	10		15
9			4Å	S	22		57
10			5Å	S	18		11
11			13X	S	39		62

[a] One g of sieves/mmol of diene 1. [b] Determined according to ref 10. [c] Yield after chromatography. [d] Determined by GC on SE-30-type columns.

when the chiral acids were employed. Addition of molecular sieves lowered the yields even further. One reason for this could be that the diene **1** was consumed more rapidly in the presence of molecular sieves, as shown by GC. Attempts to improve the yield in the reactions with molecular sieves by omitting the MnO_2 and instead using *p*-benzoquinone as the only reoxidant, thereby avoiding two solid phases, failed. Instead, when the nucleophile **15** was used together with Lancaster 13X (1 mmol scale) and 1.2 equiv of benzoquinone, the yield was lowered (14–21%) while the de remained the same as for the ordinary reoxidation system.

Amount of Molecular Sieves. The amount of added molecular sieves Lancaster 13X was varied for the two nucleophiles **14** and **15** to see how the selectivity was affected (Table III). Addition of 0.5 g of Lancaster 13X to a reaction mixture (1 mmol of diene **1**, 5 mmol of nucleophile) with the *o*-phenyl-substituted acid **14** both increased the stereoselectivity and reversed the absolute configuration of the major diastereomer (entries 1 and 2). Further increase in the amount of molecular sieves to 1 and 2 g resulted in de values of 43% and 56%, respectively. For the disubstituted acid **15**, which gave a 17% de without molecular sieves, only a 14% improvement in de was observed when the amount of molecular sieves was increased from 1 to 3 g (from 62 to 76%).

Different Kinds of Molecular Sieves. Different kinds of molecular sieves were also tried for the chiral acids **14** and **15** (Table IV). The best selectivity was observed for the sieves Lancaster 4 Å and 13X. Both have sodium as counterion, which possibly suggests a favorable influence of the counterion (vide infra). Use of the hydrophobic molecular sieves USY, which consist entirely of SiO_2, gave no effect, and the molecular sieves NaY resulted in low selectivity.[11a,b]

Influence of Solvent. The influence of solvent was

(10) The absolute configuration was determined by hydrolysis of the diastereomers, measurement of the optical rotation of the alcohol, and esterification with *O*-methylmandelic acid. (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512. (b) Roy, B. L.; Deslongchamps, P. *Can. J. Chem.* **1985**, *63*, 651. (c) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M. *J. Org. Chem.* **1986**, *51*, 2370.

(11) (a) Three materials (13X, 4-, and 5-Å sieves) were analyzed by electron microscopy. The results show that the 13X and 4-Å sieves contain some Na^+. No other metals including transition metals were detected. (b) The acidity of the sieves may possibly have an influence on the selectivity. However, this has not been studied. (c) The molecular sieves were dried by heating them to 400 °C for 3–4 h. The loss of weight, corresponding to the water content, was found to be approximately 20% for Lancaster 13X, 3, 4, and 5Å. The sieves USY contained 1.4% water, and NaY contained 29% water.

investigated in two reactions with the chiral acid 15 together with Lancaster 13X, where acetone was replaced by CH_2Cl_2 and THF. When CH_2Cl_2 was used, the de dropped to 41% (34% yield) while the choice of THF as solvent did not change the selectivity (62% de, 31% yield). In both cases, the major diastereomer had *S* configuration at C7.

Effect of Water. The effect of water on the selectivity was investigated in order to ascertain if the molecular sieves serve to eliminate moisture, thereby preventing the catalyst from being spoiled by water. However, it turned out that use of dehydrated sieves lowered the selectivity considerably, whereas sieves containing 20% water improved the diastereomeric excess as reported above.[11c] For example, when the acid 16 was used together with the catalytic system and dried molecular sieves Lancaster 13X in dry acetone under nitrogen atmosphere, the de was only 3.5% (cf. Table II, entry 6). When the same reaction was run with a stoichiometric amount of *p*-benzoquinone instead of *p*-benzoquinone/MnO_2, thus completely avoiding water formation, there was no selectivity at all! Furthermore, dry sieves lowered the yields in these reactions considerably (13 and 17% yields of 33, respectively). At the present time, it seems difficult to rationalize the low yields since GC experiments showed that the diene 1 decomposed more slowly in the presence of dry molecular sieves than with water-containing sieves. A possible explanation could be that dry molecular sieves destroy the catalyst. These results clearly demonstrate that the role of the molecular sieves is not to protect the catalyst from moisture. Instead, the presence of water is actually beneficial for the stereoselectivity.

NMR Studies. In order to investigate whether absorption of the diene, the nucleophile, or both, is essential to obtain high selectivity, solid-state ^{13}C NMR of molecular sieves, which had been treated with acetone solutions of the diene and the acid 15, were studied. The ^{13}C NMR spectrum of treated Lancaster 13X showed a mixture of acid and its corresponding sodium salt, as verified by comparison with spectra of the acid and the carboxylate. On the other hand, the NMR spectrum of treated hydrophobic USY showed absorption of the acid well as the diene. Of course, no carboxylate could be formed in the latter case since these sieves contain no metal ion.

In order to check if formation of sodium carboxylate was essential for the high selectivity, solid-state ^{13}C NMR of Lancaster 3, 4, and 5 Å, treated as above, were studied. The spectra showed carboxylic acid only. Moreover, IR spectra of the evaporated acetone solutions from these experiments and from the experiment with Lancaster 13X showed only carboxylic acid, demonstrating that the sodium carboxylate, when formed, is adsorbed on the sieves exclusively.

If the formation of a sodium carboxylate accounts for the high selectivity when a chiral acid is used as nucleophile in the presence of molecular sieves, it should be possible to use a preformed carboxylate with equal success. However, when the acid 15 was replaced by its corresponding sodium salt, and the ordinary reoxidation system, without molecular sieves, was used, no product was formed. The same negative result was observed with the carboxylate together with Lancaster 13X and also when a mixture of carboxylic acid and carboxylate was used in a ratio of 1/1. Moreover, use of sodium carboxylate in the presence of a stoichiometric amount of $Pd(OAc)_2$ gave no product.[12]

An attempt to see if prolonged time for adsorption of the nucleophile on the sieves could result in enhanced selectivity was made by stirring the acid 15 and Lancaster 13X in acetone for 48 h before the diene 1 and the catalytic system were added (standard conditions). However, no improved selectivity was observed.

Reactions in the Presence of SiO_2 and AlO_4. Since molecular sieves are composed of SiO_4 and AlO_4 we wished to check if the presence of these oxides alone would affect the stereoselectivity of the cyclization reaction. Therefore, a reaction with (*R*)-2-(2-fluorophenoxy)propionic acid (12) as nucleophile was run in the presence of silica gel and another reaction run with (*R*)-2-(2,4-dichlorophenoxy)-propionic acid (15) in the presence of Al_2O_3. The selectivity, however, was low in both cases (6% de and the diastereomer with 7*S* configuration predominating in both reactions). Although it can be argued that the particle size of the oxides in the above reactions was larger than that of the sieves ordinarily used, the fact that low selectivity was also observed with the molecular sieves USY (Table IV), which consist entirely of SiO_2, suggests that the explanation is to be found elsewhere.

Chiral Catalyst. In order to study the influence of molecular sieves on the catalyst, $Pd(OAc)_2$ was stirred with 2 equiv of (*R*)-2-(2,4-dichlorophenoxy)propionic acid (15) in dry deuterated chloroform with and without Lancaster 13X. It was found that free acid 15 remained after 24 h in the absence of molecular sieves whereas no free 15 was detected in the presence of molecular sieves. However, when the complex obtained from the latter reaction was used as catalyst, either using the chloroform solution after having filtered off the molecular sieves or using the solid complex after having evaporated the filtered chloroform solution in order to get rid of acetic acid, together with 15 and *p*-benzoquinone/MnO_2, the de was of the same order of magnitude as for the reaction run with $Pd(OAc)_2$ and no molecular sieves.

The NMR spectrum of the above-mentioned complex was very complicated. The reason for this was thought to be incomplete substitution of acetate in the trimeric structure,[13] a fact which may also explain the low induction in the cyclization reaction. Therefore, a chiral complex was prepared from $Pd(OAc)_2$ and an excess of 15,[14] and indeed this resulted in a simpler NMR spectrum. However, reaction of 15 and *cis*-1,2-divinylcyclohexane (1) with this catalyst, *p*-benzoquinone, and MnO_2 in acetone did not result in improved selectivity. Thus, the more efficient formation of a chiral palladium carboxylate in the presence of molecular sieves is not the entire explanation for the enhanced induction in the cyclization reaction.

$Pd(OAc)_2$ was found to have a strong affinity for the sieves, since it remained adsorbed even after Soxhlet extraction with acetone. The adsorbed palladium complex was inactive in the cyclization since an attempt to use $Pd(OAc)_2$ adsorbed on Lancaster 13X as catalyst together with the ordinary reoxidation system failed. The strong affinity of the catalyst for the sieves might account for the low yields in these reactions (vide supra).

Discussion

Zeolites, a kind of molecular sieves, are crystalline microporous aluminosilicates with a three-dimensional framework containing cavities and channels of molecular

(12) The sodium salt probably reacts to yield a σ,π-palladium complex analogous to previous examples: Paiaro, G.; De Renzi, A.; Palumbo, R. *J. Chem. Soc., Chem. Commun.* **1967**, 1150.

(13) Maitlis, P. M.; Espinet, P.; Russel, M. J. H. In *Comprehensive Organometallic Chemistry*; Pergamon: New York, 1982; Vol. 6, p 239.

(14) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

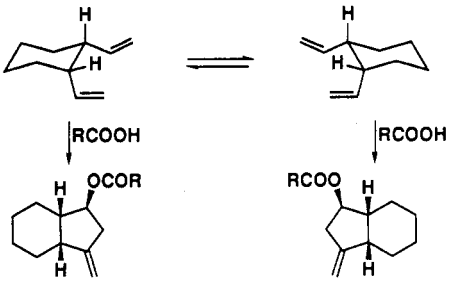
dimensions, 3–10 Å.[15] The polymeric framework consists of AlO_4 and SiO_4 tetrahedra linked by shared oxygen atoms. The incorporation of aluminum in the zeolite framework results in a negative charge, which is compensated by a cation, usually Na^+, K^+, or Ca^{2+}. The cation is relatively mobile and can be exchanged for other cations. The pores normally contain water of hydration which can be removed by heating without causing collapse of the three-dimensional network. Dehydrated zeolites are able to absorb water as well as organic compounds. The latter are preferentially absorbed by hydrophobic molecular sieves such as USY, which is composed of SiO_2 solely.

The effect of molecular sieves in the epoxidation of allylic alcohols has been ascribed to its water-trapping properties, since water has been shown to lower both the enantioselectivity and the reaction rate by interacting both reversibly and irreversibly with the catalyst.[1] However, the results presented in this paper clearly demonstrate that the role of the molecular sieves in the palladium-catalyzed oxidative cyclization is not to eliminate water from the reaction system. In contrast, the presence of water is crucial for the selectivity as well as for the yields.

The composition and structure of the zeolite are clearly important, since different results were obtained with different kinds of molecular sieves. These results cannot only be explained by the differences in pore size, since 4-Å sieves result in higher selectivities than both 5- and 3-Å sieves. Instead, the counterion appears to be of some importance since the best selectivity was observed using sieves with high sodium content (4 Å: Na/Si = 1/1, 13X: Na/Si ≈ 0.8/1, NaY: Na/Si ≈ 0.4/1), whereas those containing potassium or calcium (3 and 5 Å, respectively) gave rise to only a slight effect. Such effect of the counterion was not observed in the titanium-catalyzed Diels–Alder reaction or in the Sharpless epoxidation, in which 3-, 4-, and 5-Å sieve powders showed a positive influence whereas in the former case Lancaster 13X sieves had no effect.[1,2] An effect of a counterion may be rationalized by considering a conformational effect involving interaction of the cation with the oxygen atom linked to the aromatic ring, which would result in a more rigid nucleophile with higher steric requirements. Unfortunately, the reaction using (*R*)-3-phenylpropionic acid, which lacks an oxygen atom adjacent to the aromatic ring, could not be used to judge whether chelate formation has any effect, since this acid gave the product in low yield, and the diastereomers were obtained in essentially equal amounts even in the presence of sieves Lancaster 13X. However, as shown by ^{13}C NMR spectra of the solid zeolites, the formation of sodium carboxylate is not essential for high selectivity, since the salt was not formed on 4-Å sieves, and use of these resulted in good selectivity.

Mechanistic studies have demonstrated that palladium–diene complexes are intermediates in the oxidative cyclization.[16] Furthermore, it has been shown that only nucleophilic attack on the equatorial olefinic bond of dichloro(η^4-*cis*-1,2-divinylcyclohexane)palladium leads to product and that the selectivity resides in the nucleophilic attack (Scheme I).[17,18] It therefore seems realistic that

Scheme I



any factor that can favor one of the two enantiomeric chair conformations of the divinylcyclohexane would be beneficial for high selectivity.

The formation of a chiral palladium complex may well result in unequal formation of the cyclohexane conformers, which would lead to products whose stereochemistry differs from those obtained from nonchiral acetate complexes and chiral nucleophiles. We were indeed able to demonstrate that the equilibrium between palladium acetate and (*R*)-2-(2,4-dichlorophenoxy)propionic acid was driven toward chiral palladium carboxylate formation in the presence of molecular sieves Lancaster 13X, probably due to the absorption of acetic acid in the sieves. ^1H NMR experiments demonstrated that chiral palladium complexes which probably consisted of trimers containing chiral carboxylate as well as acetate were formed faster in the presence of sieves 13X, 4, and 5 Å; the spectra also showed that acetic acid was absent or present in only trace amounts. That acetic acid could be absorbed in the sieves was demonstrated by solid-state ^{13}C NMR spectroscopy. Improved formation of a chiral catalyst was shown to be responsible for the effect of molecular sieves in the titanium-catalyzed glyoxylate–ene reaction in which the sieves facilitated ligand exchange.[3b] In this case only a small amount of sieves was required to achieve high selectivity when a catalytic amount of the titanium complex was used. If this facilitated formation of a chiral catalyst were to be the explanation for the effect of the molecular sieves also in our palladium-catalyzed reaction, it seems reasonable that sieves with pore diameter 3 Å have no effect, since acetic acid is too bulky to enter the pores. However, this does not explain why 5-Å sieves are less efficient than the smaller 4-Å sieves and that such large amounts of sieves are required. Furthermore, using a chiral palladium carboxylate as catalyst did not result in increased selectivity compared to reactions run without molecular sieves.

Absorption of some of the reagents on the molecular sieves can be expected to change their conformation. However, absorption of the diene is clearly shown, by solid-state ^{13}C NMR spectroscopy, not to be involved, since the diene is absorbed only on the sieves USY that give rise to no effect at all. That absorption of the nucleophile has an effect on the selectivity cannot, however, be ruled out, the enhanced selectivity being explained by a larger energy difference between the diastereomeric transition states using a nucleophile absorbed on the macromolecular framework. Sodium may act as a stronger absorption center than potassium and calcium, since the latter are screened by the oxygen atoms to a larger extent,[15c] thereby explaining the beneficial effect of a high sodium level of the sieves. The formation of products with *S* configuration at the newly formed chiral center from all nucleophiles in the presence of molecular sieves could be explained by similar conformations of all nucleophiles in the presence

(15) (a) Hölderich, W.; Hesse, M.; Näumann, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 226. (b) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*; Structure Commission of the International Zeolite Association, 1978. (c) Zhdanov, S. P.; Khvoshchev, S. S.; Feoktistova, N. N. *Synthetic Zeolites*; Gordon and Breach Science Publishers: New York, 1990; Vol. II. (d) van Bekkum, H.; Kouwenhoven, H. W. *Rec. Trav. Chim. Pays-Bas* **1989**, *108*, 283.

(16) Moberg, C.; Sutin, L.; Heumann, A. *Acta Chem. Scand.* **1991**, *45*, 77.

(17) Moberg, C.; Sutin, L.; Csöregh, I.; Heumann, A. *Organometallics* **1990**, *9*, 974.

(18) Moberg, C.; Sutin, L. *Acta Chem. Scand* **1992**, *46*, 1000.

of molecular sieves, favoring nucleophilic attack on the *si* side of the diene. A surface effect was, indeed, observed in that the diastereomeric product esters were adsorbed on the molecular sieves to different extents. This was found when the products were isolated, since filtration followed by repeated washing of the sieves after reaction yielded the isomers in ratios different from those observed when the products were isolated quantitatively by Soxhlet extraction.[19,20] The involvement of a surface effect is also suggested by the quite large amount of sieves required to achieve high selectivity.

Summary

We have found that the presence of molecular sieves Lancaster 13X and 4 Å increase the stereoselectivity in the palladium-catalyzed oxidative cyclization of *cis*-1,2-divinylcyclohexane with chiral acids. The substituents of the acid have an important influence on the stereochemical outcome of the reaction, and only nondried molecular sieves increase the stereoselectivity. Therefore, the effect of the molecular sieves cannot be due to their water-trapping properties. A chiral catalyst was formed faster in the presence of molecular sieves, but this is not the only explanation for the improved stereoselectivity in the cyclization. Molecular sieves with a high sodium content have a favorable effect on the selectivity, possibly suggesting that absorption of the nucleophile is important. A further possibility, which has not yet been investigated, is that the molecular sieves influence the relative rates of the reaction steps (reversible addition of palladium carboxylate, rate-determining insertion, β-elimination), thereby affecting the initial equilibrium. A complete understanding of the beneficial influence of the molecular sieves remains unclear. However, it is different from the explanations offered for the previously reported reactions run in the presence of molecular sieves, since it is not due only to the trapping of a small molecule in the pore system of the zeolite.

Experimental Section

General Methods. ^1H NMR and ^{13}C NMR were recorded on 100-, 200-, 250-, and 400-MHz spectrometers (^{13}C NMR: 25.1, 50.3, 62.9 and 100.6 MHz). ^1H NMR spectra were recorded in $CDCl_3$ with Me_4Si as internal standard. ^{13}C NMR spectra were recorded in $CDCl_3$ ($CDCl_3$ δ 77.0 as internal standard). Analytical GC was performed on SE-30 type columns. Melting points were measured on a Büchi 510 apparatus and are uncorrected. Chromatography on silica gel was performed according to ref 21. When conventional flash chromatography[22] was used the products were often contaminated by an impurity. The presence of this impurity did not affect the measurement of the diastereomeric excess. By "in vacuo" is meant a rotary evaporator operating at water aspirator pressure.

Materials. Palladium(II) acetate was purchased from Engelhardt, and *cis*-1,2-divinylcyclohexane, L-(+)-lactic acid and (*S*)-(+)-*O*-methoxymandelic acid were purchased from Fluka, (*S*)-(−)-ethyl lactate, *p*-benzoquinone, and MnO_2 from Merck, (*S*)-(−)-methyl lactate, (*R*)-(+)-isobutyl lactate, (*S*)-(+)-*O*-acetylmandelic acid, acetyl chloride, isobutyryl chloride, DEAD, triphenylphosphine, 2-fluorophenol, 4-fluorophenol, and 2-phenylphenol from Aldrich, and (*S*)-(+)-mandelic acid and (1*S*)-(−)-camphanic acid from Janssen. (*R*)-(−)-*O*-acetylmandelic acid was synthesized according to a literature procedure.[23] Molecular sieve powders 3, 4, 5 Å, and 13X from Lancaster were used as received. *p*-Benzoquinone, 4-chloro-2-methylphenol, 2-fluorophenol, and 4-fluorophenol were recrystallized prior to use. Molecular sieves USY and NaY were a gift from professor Sten Andersson, University of Lund. (*R*)-2-(2,4-Dichlorophenoxy)propionic acid and (*R*)-2-(4-chloro-2-methylphenoxy)propionic acid were a gift from BASF. Hexane and ethyl acetate were distilled before use. Dry Et_2O and THF were obtained by distillation from benzophenone ketyl.

Synthesis of *O*-Acylated Acids. The acid chloride (acetyl or isobutyryl chloride) was added dropwise to L-lactic acid (neat, ratio 3:1) under stirring. The reaction mixture became warm, and HCl gas evolved. After 1 h at rt excess acid chloride was evaporated and the acid was distilled at high vacuum. The yields were fairly low due to di- and trimerization of lactic acid under the reaction conditions.

Synthesis of *O*-Arylated Lactic Acid Derivatives. The reaction was performed under N_2 atmosphere. A solution of DEAD (110 mmol) in THF (75 mL) was added dropwise during 1 h to a mixture of (*S*)-methyl or ethyl lactate (100 mmol), the substituted phenol (100 mmol), and triphenylphosphine (100 mmol) in THF (150 mL). The reaction mixture was subsequently stirred at ambient temperature overnight. The THF was evaporated and diethyl ether, or a mixture of diethyl ether and hexane, was added in order to precipitate the formed triphenylphosphine oxide, which was filtered off. This procedure was repeated several times. The crude product was loaded on silica gel and purified by chromatography. The obtained ester usually contained impurities which were removed during the workup procedure of the hydrolysis. **Hydrolysis:** The ester (50 mmol) was dissolved in methanol (220 mL), after which NaOH (*c* 2 M) was added (50 mL). When the reaction was complete the methanol was removed in vacuo and 50 mL of water was added. The aqueous phase was extracted with diethyl ether (3 × 50 mL), cooled with an ice bath, and neutralized with concentrated HCl. The neutralized aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were washed with brine (2 × 50 mL) and extracted with a saturated aqueous solution of Na_2CO_3 (3 × 25 mL). The combined aqueous phases were extracted with ether (3 × 25 mL), cooled with an ice bath, and neutralized with concentrated HCl. The neutralized aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were washed with brine (2 × 50 mL) and dried ($MgSO_4$). The ether was removed in vacuo, and the crude product was recrystallized from hexane.

Cyclization of *cis*-1,2-Divinylcyclohexane. General Procedure. *cis*-1,2-Divinylcyclohexane (1 mmol), the acid (5 mmol), $Pd(OAc)_2$ (0.05 mmol), *p*-benzoquinone (0.2 mmol), and MnO_2 (1.1 mmol) in acetone (6.5 mL) were stirred at ambient temperature for 2–5 days. Then 10 mL of brine was added, and the aqueous phase was extracted with hexane/EtOAc (7/3) or EtOAc (3 × 25 mL). The combined organic phases were extracted with saturated aqueous Na_2CO_3 (3 × 25 mL) and dried ($MgSO_4$). The solvent was removed in vacuo. The crude product was purified by chromatography to yield a mixture of two diastereomers. The diastereomers **21a** and **21b** were separated by medium-pressure chromatography using microcrystalline cellulose triacetate as the mobile phase (94/6 EtOH/H_2O). The diastereomers **26a** and **26b** were separated by means of semipreparative HPLC.

Cyclization with Lactic Acid. *cis*-1,2-Divinylcyclohexane (10 mmol), L-lactic acid (55–60 mmol), $Pd(OAc)_2$ (0.5 mmol), *p*-benzoquinone (1.9 mmol), and MnO_2 (10 mmol) were stirred in acetone (30 mL) for 4 days at rt to yield 1.54 g (72%) of products **20** and **23** in a ratio of 62/38 (GC). **20** and **23** were separated by conventional flash chromatography.

Cyclization of *cis*-1,2-Divinylcyclohexane in the Presence of Molecular Sieves. General Procedure. The acid (5 mmol)

(19) For example, from the *o*-phenyl nucleophile, filtration yielded the products in 17% yield in a ratio of 4.9/1, whereas a 41% yield of diastereomers in a ratio of 1.3/1 was obtained after extraction. Likewise, from the dichloro nucleophile 15, a 28% yield with a ratio of isomers of 3.3/1 and a 40% yield with a ratio of 4.6/1 were obtained after filtration and extraction, respectively. IR and solid-state ^{13}C NMR of the extracted sieves showed that no product remained absorbed.

(20) This phenomenon was recently taken advantage of in the separation of diastereomers using molecular sieves ZSM, see: Weitkamp, J.; Schäfer, K.; Ernst, S. *J. Chem. Soc., Chem. Commun.* **1991**, 1142.

(21) Baeckström, P.; Stridh, K.; Li, L.; Norin, T. *Acta Chem. Scand.* **1987**, *B41*, 442.

(22) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(23) Thayer, F. K. In *Organic Synthesis*, 2nd ed.; John Wiley & Sons: New York, 1944; Collect. Vol. I, p 12.

was dissolved in acetone (6.5 mL), the salts were added ($Pd(OAc)_2$ (0.05 mmol), *p*-benzoquinone (0.2 mmol) and MnO_2 (1.1 mmol)) followed by the powdered molecular sieves (1 g), and finally *cis*-1,2-divinylcyclohexane (1 mmol) was added. Reaction time: 2–5 days. The reaction mixture was then extracted (Soxhlet) with hexane/EtOAc (7/3) or EtOAc for 1.5 h. The organic phase was extracted with saturated aqueous Na_2CO_3 (3 × 25 mL) and dried ($MgSO_4$). The solvent was removed in vacuo. The crude product was purified by chromatography on silica gel. IR and solid-state ^{13}C NMR spectra of the extracted molecular sieves indicated that no product remained adsorbed.

(*R*)-2-Phenoxypropionic acid (11): ^1H NMR (250 MHz) δ 7.22–7.34 (m, 2 H), 6.95–7.05 (m, 1 H), 6.85–6.94 (m, 2 H), 4.80 (q, *J* = 7 Hz, 1 H), 1.67 (d, *J* = 7 Hz, 3 H); ^{13}C NMR (62.9 MHz) δ 178.42, 157.10, 129.52(2C), 121.73, 114.96(2C), 71.78, 18.28; mp 83 °C; yield 53%; $[\alpha]^{20}_D$ = 19 (*c* 1.0, $CHCl_3$).

(*R*)-2-(2-Phenylphenoxy)propionic acid (14): ^1H NMR (250 MHz) δ 7.51–7.58 (m, 2 H), 7.38–7.45 (m, 2 H), 7.26–7.38 (m, 3 H), 7.08–7.14 (m, 1 H), 6.90–6.97 (m, 1 H), 4.70 (q, *J* = 7 Hz, 1 H), 1.53 (d, *J* = 7 Hz, 3 H); ^{13}C NMR (62.9 MHz) δ 178.35, 154.04, 138.04, 131.69, 131.26, 129.46(2C), 128.47, 127.93(2C), 126.97, 122.35, 113.96, 72.70, 18.23; mp 70.5–72.5 °C; yield 59%; $[\alpha]^{20}_D$ = −5 (*c* 2.0, EtOH).

(1*R*,6*S*,7*S*)- and (1*S*,6*R*,7*R*)-7-[[(1(*S*)-hydroxyethyl)carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (20): ^1H NMR (200 MHz) δ 4.97 (m, $w_{1/2}$ = 8 Hz, 2 H, C*H*OCOR* and CH_2=C), 4.88 (q, *J* = 2.5 Hz, 1 H, CH_2=C), 4.22 (quintet, becomes q with D_2O, *J* = 7 Hz, 1 H, C*H*(OH)CH_3), 2.91 (ddq, part of AB, *J* = 19, 6.5, and 2 Hz, 1 H, C_8H_{endo}), 2.77 (2d, *J* = 5.5 Hz, 1 H, O*H*), 2.71 (br s, $w_{1/2}$ = 15 Hz, 1 H, C_1H), 2.39 and 2.42 (2d, part of AB, *J* = 19 Hz, 1 H, C_8H_{exo}), 2.09 (br s, $w_{1/2}$ = 20 Hz, 1 H, C_6H), 1.72–1.88 (m, 1 H), 1.49–1.7 (m, 3 H), 1.38 and 1.39 (2d, *J* = 7 Hz, 3 H, CHCH_3), 1.13–1.44 (m, 3 H), 0.87–1.07 (m, 1 H).

(1*R*,6*S*,7*S*)-7-[[(1(*S*)-Acetoxyethyl)carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (21a): ^1H NMR (400 MHz) δ 4.98 (q, *J* = 7 Hz, 1 H, C*H*CH_3), 4.92 (m, 1 H, CH_2=C), 4.89 (dt, *J* = 6.5 and 2.5 Hz, 1 H, C*H*OCOR*), 4.84 (q, *J* = 2 Hz, 1 H, CH_2=C), 2.85 (ddq, part of AB, *J* = 18, 6.5 and 2 Hz, 1 H, C_8H_{endo}), 2.64 (m, $w_{1/2}$ = 14 Hz, 1 H, C_1H), 2.41 (d, part of AB, *J* = 18 Hz, 1 H, C_8H_{exo}), 2.09 (s, 3 H, acetyl), 2.03 (m, $w_{1/2}$ = 14 Hz, 1 H, C_6H), 1.76 (dq, *J* = 13 and 4 Hz, 1 H), 1.47–1.61 (m, 3 H), 1.43 (d, *J* = 7 Hz, 3 H, CHCH_3), 1.27–1.37 (m, 2 H), 1.13–1.26 (m, 1 H), 0.84–0.96 (m, 1 H); ^{13}C NMR (100.6 MHz), δ 170.58, 170.29, 150.03, 106.11, 78.39, 68.75, 44.84, 41.13, 37.3, 25.47, 25.15, 24.08, 21.57, 20.58, 16.84; $[\alpha]^{22}_D$ = −39.3 (*c* 1.34, CH_2Cl_2).

(1*S*,6*R*,7*R*)-7-[[(1(*S*)-Acetoxyethyl)carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (21b): ^1H NMR (400 MHz) δ 4.96 (q, *J* = 7 Hz, 1 H, C*H*CH_3), 4.92 (m, 1 H, CH_2=C), 4.88 (dt, *J* = 6.5 and 2.5 Hz, 1 H, C*H*OCOR*), 4.84 (q, *J* = 2 Hz, 1 H, CH_2=C), 2.83 (ddq, part of AB, *J* = 18, 6.5, and 2 Hz, 1 H, C_8H_{endo}), 2.67 (m, $w_{1/2}$ = 14 Hz, 1 H, C_1H), 2.33 (d, part of AB, *J* = 18 Hz, 1 H, C_8H_{exo}), 2.08 (s, 3 H, acetyl), 2.06 (m, 1 H, hidden in part by the acetyl signal, C_6H), 1.76 (dq, *J* = 13 and 4 Hz, 1 H), 1.48–1.62 (m, 3 H), 1.41 (d, *J* = 7 Hz, 3 H, CHCH_3), 1.27–1.37 (m, 2 H), 1.13–1.25 (m, 1 H), 0.83–0.93 (m, 1 H); ^{13}C NMR (100.6 MHz) δ 170.54, 170.28, 149.98, 106.06, 78.40, 68.75, 44.74, 41.05, 37.37, 25.33, 25.14, 24.12, 21.49, 20.55, 16.75; $[\alpha]^{22}_D$ = −19.02 (*c* 1.72, CH_2Cl_2). Hydrolysis (MeOH/NaOH, 60 °C, 15 min) gave the enantiomerically pure alcohol (1*S*,6*R*,7*R*)-7-hydroxy-9-methylenebicyclo[4.3.0]nonane: $[\alpha]^{22}_D$ = 33.1 (*c* 0.4, CH_2Cl_2).

Compounds **21a** and **21b**. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.32. Found: C, 67.64; H, 8.24.

(1*R*,6*S*,7*S*)- and (1*S*,6*R*,7*R*)-7-[[[1(*S*)-[(isopropylcarbonyl)oxy]ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (22): ^1H NMR (200 MHz) δ 4.81–5.10 (m, 4 H, C*H*CH_3, C*H*OCOR*, and CH_2=C), 2.88 (ddq, part of AB, *J* = 18, 6.5, and 2 Hz, 1 H, C_8H_{endo}), 1.95–2.75 (m, 3 H), 2.6 (septet, *J* = 7 Hz, 1 H, C*H*$(CH_3)_2$), 0.8–1.9 (m, 8 H), 1.46 and 1.47 (2d, *J* = 7 Hz, 3 H, CHCH_3), 1.18 and 1.21 (2d, *J* = 7 Hz, 6 H, CH$(CH_3)_2$). Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found: C, 69.46; H. 8.98.

(1*R*,6*S*,7*S*)- and (1*S*,6*R*,7*R*)-7-[[(1(*S*)-lactoxyethyl)carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (23): ^1H NMR (200 MHz) δ 5.12 and 5.13 (2q, *J* = 7 Hz, 1 H, C*H*CH_3OCOR), 4.85–5.0 (m, 3 H, C*H*OCOR* and CH_2=C), 4.32 and 4.35 (2q, *J* = 7 Hz, 1 H, C*H*(OH)CH_3), 2.89 (d, part of AB, *J* = 18 Hz, 1 H, C_8H_{endo}), 2.61–2.77 (m, 2 H, O*H* and C_1H), 2.34 and 2.44 (2d, part of AB, *J* = 18 Hz, 1 H, C_8H_{exo}), 2.0–2.17 (m, 1 H, C_6H), 1.69–1.88 (m, 1 H), 1.1–1.68 (m, 6 H), 1.48, 1.50 and 1.51 (3d, 6 H, CHCH_3), 0.8–1.15 (m, 1 H).

(1*R*,6*S*,7*S*)- and (1*S*,6*R*,7*R*)-7-[2(*S*)-hydroxy-2-phenylacetoxy]-9-methylenebicyclo[4.3.0]nonane (24): ^1H NMR (200 MHz) δ 7.2–7.5 (m, 5 H), 5.12 (br s, $w_{1/2}$ = 4 Hz, 1 H, C*H*OH), 4.78–4.98 (m, 3 H, C*H*OCOR* and CH_2=C), 3.4 (br s, $w_{1/2}$ = 30 Hz, 1 H, O*H*), 2.78 and 2.89 (2ddq, part of AB, *J* = 18, 6.5, and 2 Hz, 1 H, C_8H_{endo}), 2.63 (m, $w_{1/2}$ = 12 Hz, 1 H, C_1H), 2.15 and 2.46 (d, part of AB, *J* = 18 Hz, 1 H, C_8H_{exo}), 0.7–1.9 (m, 9 H). Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74. Found: C, 75.85; H, 7.70.

(1*R*,6*S*,7*S*)-7-[2(*S*)-Acetoxy-2-phenylacetoxy]-9-methylenebicyclo[4.3.0]nonane (25a): ^1H NMR (400 MHz, assigned from a mixture of **25a**/**25b**) δ 7.3–7.6 (m, 5 H), 5.83 (s, 1 H, C*H*OAc), 4.92 (m, $w_{1/2}$ = 5 Hz, 1 H, CH_2=C), 4.87 (m, $w_{1/2}$ = 16.5 Hz, 1 H, C*H*OCOR*), 4.81 (m, $w_{1/2}$ = 10.5 Hz, 1 H, CH_2=C), 2.83 (ddq, part of AB, *J* = 18, 6.5, and 2 Hz, 1 H, C_8H_{endo}), 2.47 (m, 1 H, C_1H), 2.45 (d, part of AB, *J* = 18 Hz, 1 H, C_8H_{exo}), 2.17 (s, 3 H, acetyl), 1.85 (m, $w_{1/2}$ = 20 Hz, 1 H, C_6H), 1.67–1.81 (m, 1 H), 1.4–1.65 (m, 3 H), 1.06–1.4 (m, 3 H), 0.73–0.95 (m, 1 H); ^{13}C NMR (100.6 MHz) δ 170.26, 168.58, 149.96; 133.95, 129.07, 128.68, 127.48, 106.08, 78.79, 74.71, 44.65, 41.00, 37.21, 25.31, 25.01, 24.03, 21.47, 20.64.

(1*S*,6*R*,7*R*)-7-[2(*S*)-Acetoxy-2-phenylacetoxy]-9-methylenebicyclo[4.3.0]nonane (25b): ^1H NMR (400 MHz, assigned from a mixture of **25a**/**25b**) δ 7.3–7.6 (m, 5 H), 5.82 (s, 1 H, C*H*OAc), 4.92 (m, $w_{1/2}$ = 5 Hz, 1 H, CH_2=C), 4.87 (m, $w_{1/2}$ = 16.5 Hz, 1 H, C*H*OCOR*), 4.81 (m, $w_{1/2}$ = 10.5 Hz, 1 H, CH_2=C), 2.74 (ddq, part of AB, *J* = 18, 6.5 and 2 Hz, 1 H, C_8H_{endo}), 2.66 (m, $w_{1/2}$ = 14 Hz, 1 H, C_1H), 2.45 (d, part of AB, *J* = 18 Hz, 1 H, C_8H_{exo}), 2.17 (s, 3 H, acetyl), 2.10 (m, $w_{1/2}$ = 25 Hz, 1 H, C_6H), 1.67–1.81 (m, 1 H), 1.4–1.65 (m, 3 H), 1.06–1.4 (m, 3 H), 0.73–0.95 (m, 1 H); ^{13}C NMR (100.6 MHz) δ 170.26, 168.58, 149.96, 133.82, 129.07, 128.68, 127.43, 105.99, 78.79, 74.73, 44.71, 41.03, 37.11, 25.31, 25.11, 24.11, 21.49, 20.64.

(1*R*,6*S*,7*S*)- and (1*S*,6*R*,7*R*)-7-[2(*S*)-Acetoxy-2-phenylacetoxy]-9-methylenebicyclo[4.3.0]nonane (25). Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.14; H, 7.36. Found: C, 73.26; H, 7.28.

(1*R*,6*S*,7*S*)-7-[2(*S*)-Methoxy-2-phenylacetoxy]-9-methylenebicyclo[4.3.0]nonane (26a): ^1H NMR (200 MHz) δ 7.29–7.47 (m, 5 H), 4.78–4.97 (m, 3 H, C*H*OCOR* and CH_2=C), 4.71 (s, 1 H, C*H*OCH_3), 3.40 (s, 3 H, OCH_3), 2.86 (ddq, part of AB, *J* = 18, 6, and 2 Hz, 1 H, C_8H_{endo}), 2.52 (m, $w_{1/2}$ = 16 Hz, 1 H, C_1H), 2.39 (d, part of AB, *J* = 18 Hz, 1 H, C_8H_{exo}), 1.8–1.94 (m, 1 H, C_6H), 1.62–1.8 (m, 1 H), 1.05–1.62 (m, 6 H), 0.71–0.98 (m, 1 H).

(1*S*,6*R*,7*R*)-7-[2(*S*)-Methoxy-2-phenylacetoxy]-9-methylenebicyclo[4.3.0]nonane (26b): ^1H NMR (200 MHz) δ 7.29–7.47 (m, 5 H), 4.78–4.97 (m, 3 H, C*H*OCOR* and CH_2=C), 4.72 (s, 1 H, C*H*OCH_3), 3.40 (s, 3 H, OCH_3), 2.78 (ddq, part of AB, *J* = 18, 6, and 2 Hz, 1 H, C_8H_{endo}), 2.59–2.72 (m, 1 H, C_1H), 2.18 (d, part of AB, *J* = 18 Hz, 1 H, C_8H_{exo}), 2.02–2.12 (m, 1 H, C_6H), 1.65–1.83 (m, 1 H), 1.05–1.65 (m, 6 H), 0.8–1.05 (m, 1 H).

(1*R*,6*S*,7*S*)- and (1*S*,6*R*,7*R*)-7-[[(2-carbonyl-3-oxa-4-(*R*)-bornyl)carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (27): ^1H NMR (400 MHz) δ 4.99 (dt, *J* = 6.5 and 6.0 Hz, 1 H, C*H*OCOR*), 4.85 and 4.94 (2m, $w_{1/2}$ = 6.5 and 2.5 Hz, 2 H, CH_2=C), 2.90 (d, part of AB, 1 H, *J* = 18 Hz, C_8H_{endo}), 2.71 (m, $w_{1/2}$ = 17 Hz, 1 H, C_1H), 2.33–2.46 (m, 2 H, C_8H_{exo} and one "camphanic" proton), 2.08 (m, $w_{1/2}$ = 20 Hz, 1 H, C_6H), 1.93–2.04 (m, 1 H), 1.82–1.92 (m, 1 H), 1.73–1.82 (m, 1 H), 1.51–1.69 (m, 4 H), 1.14–1.38 (m, 3 H), 0.85–0.98 (m, 1 H), 1.09 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3), 0.92 and 0.93 (2s, 3 H, CH_3); ^{13}C NMR (100.6 MHz) δ 178.20, 167.20, 149.58, 106.40 or 106.34, 91.02, 78.90, 54.80, 54.06, 44.93 or 44.90, 41.12, 37.66 or 37.62, 30.55 or 30.49, 28.96 or 28.93, 25.41, 25.35, 25.19 or 24.12, 21.49, 16.82, 16.74 or 16.72, 9.66. Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.28; H, 8.46.

(1*R*,6*S*,7*S*)-7-[[((*R*)-1-Phenoxyethyl)carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (28a): ^1H NMR (400 MHz, assigned from a mixture of **28a**/**28b**) δ 7.22–7.29 (m, 2 H), 6.92–6.99 (m, 1 H), 6.88–6.90 (m, 2 H), 4.82–4.99 (m, 3 H, CH_2=C and C*H*OCOR*), 4.68–4.78 (m, 1 H, C*H*CH_3), 2.82 (ddq, *J* = 18, 7 and 2 Hz, 1 H, C_8H_{endo}), 2.66 (br s, 1 H, C_1H), 2.28 (br d, *J* = 18 Hz,

1 H, C_8H_{exo}), 2.08 (br s, 1 H, C_6H), 1.66–1.82 (m, 1 H), 1.59 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.40–1.66 (m, 3 H), 1.02–1.40 (m, 3 H), 0.76–1.02 (m, 1 H).

(1*S*,6*R*,7*R*)-7-[[((*R*)-1-Phenoxyethyl)carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (28b): ^{1}H NMR (400 MHz, assigned from a mixture of **28a/28b**) δ 7.22–7.29 (m, 2 H), 6.92–6.99 (m, 1 H), 6.88–6.90 (m, 2 H), 4.82–4.99 (m, 3 H, CH_2=C and CHOCOR*), 4.68–4.78 (m, 1 H, $CHCH_3$), 2.86 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.49 (br s, 1 H, C_1H), 2.41 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 1.94 (br s, 1 H, C_6H), 1.66–1.82 (m, 1 H), 1.60 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.40–1.66 (m, 3 H), 1.02–1.40 (m, 3 H), 0.76–1.02 (m, 1 H). **28a and 28b**: ^{13}C NMR (100.6 MHz) δ 172.00, 157.56, 149.88, 129.42(2C), 121.44, 115.02(2C), 106.07, 78.21, 72.52, 44.73, 40.96, 37.23, 25.32, 25.10, 24.06, 21.46, 18.44.

(1*R*,6*S*,7*S*)-7-[[[(*R*)-1-(2-Fluorophenoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (29a): ^{1}H NMR (400 MHz, assigned from a mixture of **29a/29b**) δ 6.86–7.13 (m, 4 H), 4.82–4.97 (m, 3 H, CH_2=C and CHOCOR*), 4.70–4.79 (m, 1 H, $CHCH_3$), 2.83 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.66 (br s, 1 H, C_1H), 2.28 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 2.07 (br s, 1 H, C_6H), 1.63 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.68–1.83 (m, 1 H), 1.45–1.68 (m, 3 H), 1.13–1.40 (m, 3 H), 0.80–1.00 (m, 1 H).

(1*S*,6*R*,7*R*)-7-[[[(*R*)-1-(2-Fluorophenoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (29b): ^{1}H NMR (400 MHz, assigned from a mixture of **29a/29b**) δ 6.86–7.13 (m, 4 H), 4.82–4.97 (m, 3 H, CH_2=C and CHOCOR*), 4.70–4.79 (m, 1 H, $CHCH_3$), 2.88 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.53 (br s, 1 H, C_1H), 2.40 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 1.96 (br s, 1 H, C_6H), 1.64 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.68–1.83 (m, 1 H), 1.45–1.68 (m, 3 H), 1.13–1.40 (m, 3 H), 0.80–1.00 (m, 1 H). **29b and 29b**: ^{13}C NMR δ 171.45, 153.08 or 152.97 (d, J = 246 Hz), 149.84 or 149.73, 145.55 (d, J = 10 Hz), 124.11 or 124.13 (d, J = 3 Hz), 122.46 or 122.33 (d, J = 7 Hz), 117.21, 116.53 (d, J = 18 Hz), 106.09, 78.35, 74.45 or 74.25, 44.76 or 44.67, 40.93, 37.28 or 37.19, 25.29 or 25.25, 25.09 or 25.00, 24.11 or 24.03, 21.42, 18.42; HRMS (mixture of **29a/29b**) calcd for $C_{19}H_{24}FO_3$ 319.1710, found 319.1724.

(1*R*,6*S*,7*S*)-7-[[[(*R*)-1-(4-Fluorophenoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (30a): ^{1}H NMR (400 MHz, assigned from a mixture of **30a/30b**) δ 6.90–7.00 (m, 2 H), 6.78–6.86 (m, 2 H), 4.82–4.98 (m, 3 H, CH_2=C and CHOCOR*), 4.61–4.71 (m, 1 H, $CHCH_3$), 2.83 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.66 (br s, 1 H, C_1H), 2.27 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 2.07 (br s, 1 H, C_6H), 1.70–1.86 (m, 1 H), 1.58 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.45–1.68 (m, 3 H), 1.15–1.40 (m, 3 H), 0.80–1.00 (m, 1 H); ^{13}C NMR (100.6 MHz, assigned from a mixture of **30a/30b**) δ 171.80, 157.63 (d, J = 237 Hz), 153.68, 149.69, 116.42 (d, J = 18 Hz, 2 C), 115.80 (d, J = 23 Hz, 2 C), 106.16, 78.37, 73.44, 44.71, 41.01, 37.28, 25.30, 25.10, 24.10, 21.42, 18.40.

(1*S*,6*R*,7*R*)-7-[[[(*R*)-1-(4-Fluorophenoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (30b): ^{1}H NMR (400 MHz, assigned from a mixture of **30a/30b**) δ 6.90–7.00 (m, 2 H), 6.78–6.86 (m, 2 H), 4.82–4.98 (m, 3 H, CH_2=C and CHOCOR*), 4.61–4.71 (m, 1 H, $CHCH_3$), 2.87 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.51 (br s, 1 H, C_1H), 2.40 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 1.95 (br s, 1 H, C_6H), 1.70–1.86 (m, 1 H), 1.59 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.45–1.68 (m, 3 H), 1.15–1.40 (m, 3 H), 0.80–1.00 (m, 1 H); ^{13}C NMR (100.6 MHz, assigned from a mixture of **30a/30b**) δ 171.85, 157.63 (d, J = 237 Hz), 153.68, 149.84, 116.26 (d, J = 18 Hz, 2 C), 115.80 (d, J = 23 Hz, 2 C), 106.16, 78.30, 73.28, 44.79, 40.92, 37.21, 25.30, 25.01, 24.04, 21.45, 18.45; HRMS (mixture of **30a/30b**) calcd for $C_{19}H_{24}FO_3$ 319.1710, found 319.1752.

(1*R*,6*S*,7*S*)-7-[[[(*R*)-1-(2-Phenylphenoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (31a): ^{1}H NMR (400 MHz, assigned from a mixture of **31a/31b**) δ 7.56–7.66 (m, 2 H), 7.18–7.44 (m, 5 H), 7.01–7.08 (m, 1 H), 6.83–6.90 (m, 1 H), 4.80–4.99 (m, 3 H, CH_2=C and CHOCOR*), 4.70 (q, J = 7 Hz, 1 H, $CHCH_3$), 2.81 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.62 (br s, 1 H, C_1H), 2.25 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 2.05 (br s, 1 H, C_6H), 1.67–1.83 (m, 1 H), 1.46 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.10–1.67 (m, 6 H), 0.76–0.97 (m, 1 H).

(1*S*,6*R*,7*R*)-7-[[[(*R*)-1-(2-Phenylphenoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (31b): ^{1}H NMR (400 MHz, assigned from a mixture of **31a/31b**) δ 7.56–7.66 (m, 2 H), 7.18–7.44 (m, 5 H), 7.01–7.08 (m, 1 H), 6.83–6.90 (m, 1 H), 4.80–4.99 (m, 3 H, CH_2=C and CHOCOR*), 4.66 (q, J = 7 Hz, 1 H, $CHCH_3$), 2.85 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.44 (br s, 1 H, C_1H), 2.38 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 1.92 (br s, 1 H, C_6H), 1.67–1.83 (m, 1 H), 1.48 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.10–1.67 (m, 6 H), 0.76–0.97 (m, 1 H).

(1*R*,6*S*,7*S*)-7-[[[(*R*)-1-(2,4-Dichlorophenoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (32a): ^{1}H NMR (400 MHz, assigned from a mixture of **32a/32b**) δ 7.35–7.40 (m, 1 H), 7.09–7.16 (m, 1 H), 6.75–6.82 (m, 1 H), 4.82–5.02 (m, 3 H, CH_2=C and CHOCOR*), 4.66–4.77 (m, 1 H, $CHCH_3$), 2.83 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.65 (br s, 1 H, C_1H), 2.27 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 2.07 (br s, 1 H, C_6H), 1.71–1.89 (m, 1 H), 1.65 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.45–1.71 (m, 3 H), 1.13–1.45 (m, 3 H), 0.80–1.00 (m, 1 H); ^{13}C NMR (100.6 MHz, assigned from a mixture of **32a/32b**) δ 171.00, 152.30, 149.57, 130.24, 127.38, 127.01, 124.80, 116.13, 106.24, 78.67, 74.45, 44.82, 40.97, 37.32, 25.29, 25.13, 24.13, 21.41, 18.27.

(1*S*,6*R*,7*R*)-7-[[[(*R*)-1-(2,4-Dichlorophenoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (32b): ^{1}H NMR (400 MHz, assigned from a mixture of **32a/32b**) δ 7.35–7.40 (m, 1 H), 7.09–7.16 (m, 1 H), 6.75–6.82 (m, 1 H), 4.82–5.02 (m, 3 H, CH_2=C and CHOCOR*), 4.66–4.77 (m, 1 H, $CHCH_3$), 2.87 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.52 (br s, 1 H, C_1H), 2.40 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 1.95 (br s, 1 H, C_6H), 1.71–1.89 (m, 1 H), 1.65 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.45–1.71 (m, 3 H), 1.13–1.45 (m, 3 H), 0.80–1.00 (m, 1 H); ^{13}C NMR (100.6 MHz, assigned from a mixture of **32a/32b**) δ 171.00, 152.30, 149.70, 130.24, 127.35, 126.92, 124.74, 115.92, 106.24, 78.58, 74.32, 44.71, 40.94, 37.22, 25.29, 25.04, 24.05, 21.45, 18.32; HRMS (mixture of **32a/32b**) calcd for $C_{19}H_{22}O_3Cl_2$ 368.0946, found 368.0905.

(1*R*,6*S*,7*S*)-7-[[[(*R*)-1-(4-Chloro-2-methylphenoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (33a): ^{1}H NMR (400 MHz, assigned from a mixture of **33a/33b**) δ 7.08–7.16 (m, 1 H), 6.99–7.08 (m, 1 H), 6.56–6.64 (m, 1 H), 4.82–5.08 (m, 3 H, CH_2=C and CHOCOR*), 4.64–4.74 (m, 1 H, $CHCH_3$), 2.81 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.65 (br s, 1 H, C_1H), 2.27 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 2.23 (s, 3 H), 2.05 (br s, 1 H, C_6H), 1.70–1.86 (m, 1 H), 1.60 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.44–1.70 (m, 3 H), 1.10–1.44 (m, 3 H), 0.77–1.02 (m, 1 H).

(1*S*,6*R*,7*R*)-7-[[[(*R*)-1-(4-Chloro-2-methylphenoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (33b): ^{1}H NMR (400 MHz, assigned from a mixture of **33a/33b**) δ 7.08–7.16 (m, 1 H), 6.99–7.08 (m, 1 H), 6.56–6.64 (m, 1 H), 4.82–5.08 (m, 3 H, CH_2=C and CHOCOR*), 4.64–4.74 (m, 1 H, $CHCH_3$), 2.86 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.47 (br s, 1 H, C_1H), 2.39 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 2.23 (s, 3 H), 1.92 (br s, 1 H, C_6H), 1.70–1.86 (m, 1 H), 1.59 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.44–1.70 (m, 3 H), 1.10–1.44 (m, 3 H), 0.77–1.02 (m, 1 H).

(1*R*,6*S*,7*S*)-7-[[[(*R*)-1-(α-Naphthoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (35a): ^{1}H NMR (400 MHz, assigned from a mixture of **35a/35b**) δ 8.30–8.39 (m, 1 H), 7.75–7.82 (m, 1 H), 7.42–7.52 (m, 3 H), 7.28–7.35 (m, 1 H), 6.67–6.74 (m, 1 H), 4.78–4.99 (m, 4 H, CH_2=C, CHOCOR* and $CHCH_3$), 2.81 (ddq, J = 18, 7 and 2 Hz, 1 H, C_8H_{endo}), 2.59 (br s, 1 H, C_1H), 2.25 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 2.07 (br s, 1 H, C_6H), 1.74 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.63–1.81 (m, 1 H), 1.00–1.59 (m, 6 H), 0.74–0.85 (m, 1 H); ^{13}C NMR (100.6 MHz, assigned from a mixture of **35a/35b**) δ 171.94, 153.47, 149.72, 134.58, 127.29, 126.42, 125.80, 125.38, 125.24, 122.26, 121.15, 106.02, 105.78, 78.29, 73.13, 44.70, 40.93, 37.22, 25.25, 24.96, 24.09, 21.42, 18.45.

(1*S*,6*R*,7*R*)-7-[[[(*R*)-1-(α-Naphthoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (35b): ^{1}H NMR (400 MHz, assigned from a mixture of **35a/35b**) δ 8.30–8.39 (m, 1 H), 7.75–7.82 (m, 1 H), 7.42–7.52 (m, 3 H), 7.28–7.35 (m, 1 H), 6.67–6.74 (m, 1 H), 4.78–4.99 (m, 4 H, CH_2=C, CHOCOR*, and $CHCH_3$), 2.86 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.41 (br s, 1 H, C_1H), 2.40 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 1.86 (br s, 1 H, C_6H), 1.73 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.63–1.81 (m, 1 H), 1.00–1.59 (m, 6 H), 0.85–1.00 (m, 1 H); ^{13}C NMR (100.6 MHz, assigned from a mixture of **35a/35b**) δ 171.89, 153.47, 149.90, 134.58, 127.29, 126.42, 125.80, 125.38, 125.24, 122.26, 121.08, 106.02, 105.69, 78.18, 73.06, 44.70, 40.86, 37.22, 25.25, 25.09, 24.01, 21.42, 18.51; HRMS (mixture of **35a/35b**) calcd for $C_{23}H_{26}O_3$ 350.1881, found 350.1915.

(1*R*,6*S*,7*S*)-7-[[[(*R*)-1-(β-Naphthoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (36a): ^{1}H NMR (400

MHz, assigned from a mixture of **36a/36b**) δ 7.64–7.79 (m, 3 H), 7.39–7.46 (m, 1 H), 7.31–7.37 (m, 1 H), 7.15–7.21 (m, 1 H), 7.05–7.07 (m, 1 H), 4.79–5.00 (m, 4 H, CH_2=C, CHOCOR*, and $CHCH_3$), 2.81 (ddq, J = 18, 7, and 2 Hz, 1 H, C_8H_{endo}), 2.70 (br s, 1 H, C_1H), 2.30 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 2.10 (br s, 1 H, C_6H), 1.67 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.41–1.82 (m, 4 H), 1.00–1.41 (m, 3 H), 0.75–0.86 (m, 1 H); ^{13}C NMR (100 MHz, assigned from a mixture of **36a/36b**) δ 171.95, 155.50, 149.84, 134.22, 129.60, 129.27, 127.57, 126.70, 126.35, 123.88, 118.87, 107.65, 106.12, 78.33, 72.65, 44.84, 41.01, 37.15, 25.07, 24.97, 24.04, 21.42, 18.38.

(1*S*,6*R*,7*R*)-7-[[[(*R*)-1-(β-Naphthoxy)ethyl]carbonyl]oxy]-9-methylenebicyclo[4.3.0]nonane (36b): ^{1}H NMR (400 MHz, assigned from a mixture of **36a/36b**) δ 7.64–7.79 (m, 3 H), 7.39–7.46 (m, 1 H), 7.31–7.37 (m, 1 H), 7.15–7.21 (m, 1 H), 7.05–7.07 (m, 1 H), 4.79–5.00 (m, 4 H, CH_2=C, CHOCOR*, and $CHCH_3$), 2.85 (ddq, J = 18, 7 and 2 Hz, 1 H, C_8H_{endo}), 2.39 (br s, 1 H, C_1H), 2.44 (br d, J = 18 Hz, 1 H, C_8H_{exo}), 1.91 (br s, 1 H, C_6H), 1.66 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.41–1.82 (m, 4 H), 1.00–1.41 (m, 3 H), 0.86–1.00 (m, 1 H); ^{13}C NMR (100 MHz, assigned from a mixture of **36a/36b**) δ 172.07, 155.50, 149.67, 134.19, 129.60, 129.23, 127.54, 126.76, 126.35, 123.88, 118.81, 107.50, 106.07, 78.33, 72.65, 44.73, 40.80, 37.15, 25.03, 24.97, 24.01, 21.34, 18.43; HRMS (mixture of **36a/36b**) calcd for $C_{23}H_{26}O_3$ 350.1881, found 350.1920.

Acknowledgment. This work was supported by the Swedish Natural Science Research Council and by the Centre National de la Recherche Scientifique. We wish to thank Ms. Gurli Hammarberg for recording the IR spectra, Miss Helena Looström for performing some of the reactions with the lactic acid derivatives, and Pascal Charbonnier and Isabelle Berger for preparative work during their practical laboratory training. We are indebted to Professor Sten Andersson and Dr. Ronnie Thomasson, University of Lund, for valuable discussions about zeolites and to Mr. Heinz Kolshorn, University of Mainz, Germany, for recording some of the NMR spectra. Mass spectra were kindly recorded by Mr. Göran Lundin, Stockholm University. We thank Dr. A. Chemlal and Prof. C. Roussel for providing facilities for the separation of compounds **21a** and **21b**.

Supplementary Material Available: ^{1}H NMR for compounds **20**, **23**, **26**, **28**, **31**, and **33**, ^{13}C NMR for **28**, and spectral (^{1}H NMR) and physical data for acids **4**, **5**, **12**, **13**, and **17–19** and the methyl esters of the phenoxy acids (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Synthesis and Photochemical Rearrangement of (1*R*,7a*S*)-1-(*tert*-Butyldiphenylsiloxy)-7a-methyl-5(7a*H*)-indanone

Drury Caine* and Pravin L. Kotian

Department of Chemistry, University of Alabama, Tuscaloosa, Alabama 35487

Received June 5, 1992

Reaction of (1*S*,7a*S*)-1-hydroxy-7a-methyl-7,7a-dihydro-5(6*H*)-indanone (**5a**) with benzoic acid under the usual conditions of the Mitsunobu reaction gave a low yield of a 1:1 mixture of the benzoate derivatives **6b** and **5b** resulting from inversion and retention of configuration, respectively, at C-1. Under conditions in which the benzoic acid concentration was kept low, only the inversion product **6b** was obtained but the extent of conversion of the alcohol to the ester was low. The substitution of *p*-nitrobenzoic acid for benzoic led to a significant improvement in the yield of the inversion product **6c**. Several other methods of obtaining α-oxy derivatives of the type **6b–e** were explored but with little or no success. The reaction of the tosyloxy enone **5d** with azide ion and cyanide anion gave enones of the type **12** resulting from retention of configuration at C-1 largely or exclusively. The (*p*-nitrobenzoyl)oxy derivative **6c** was converted into the corresponding cross-conjugated cyclohexadienone, (1*R*,7a*S*)-1-(*tert*-butyldiphenylsiloxy)-7a-methyl-5(7a*H*)-indanone (**4a**), which was irradiated in glacial and in aqueous acetic acid. In the former solvent, the dienone system underwent photochemical rearrangement to give the 5/6-fused acetoxyl enone **14** and a 2:1 mixture of the tricyclic cyclopropyl ketone **15** and **16** in 25% and 17% yields, respectively, but in aqueous acetic acid phenolic products **18** and **20**, obtained by thermal cleavage of the 1,7a carbon–carbon bond, were obtained almost exclusively. In contrast, under the same photolysis conditions, the dienone **1a**, the C-1β epimer of **4a**, gave a mixture of photoproducts composed of the 5/6-fused hydroxy ketone **21**, the 5/6-fused acetoxy ketone **2a**, and the tricyclic conjugated cyclopropyl ketone **22** in 47%, 5%, and 15% yields, respectively.

Recently, the 1β-oxy-substituted 6/5-fused cross-conjugated cyclohexadienone **1a** was synthesized and converted into the 5/6-fused acetoxy enone **2a**, along with other photoproducts, by irradiation in glacial acetic acid.[1] It was felt that a similar photochemical rearrangement of the 3-isopropyl derivative of **1a**, i.e., **1b**, would produce the 5/6-fused acetoxy enone **2b**, which would be a useful precursor of the highly oxygenated oplopane sesquiterpene tussilagone (**3**)[2] and related compounds. However, the conversion of **2b** into **3** would require inversion of the configuration of the secondary oxygen functionality at C-7. Thus, it appeared of interest to prepare the C-1 epimer of dienone **1a**, i.e., **4a**, and to investigate its photochemical behavior.

The plan for the synthesis of dienone **4a** involved the application of the Mitsunobu inversion procedure[3] to the known chiral 1β-hydroxy enone **5a**[4] to give the corresponding 1α-hydroxy enone **6a**[5] followed by protection of the hydroxyl group as the *tert*-butyldiphenylsilyl derivative and oxidation of the enone to the dienone by the phenylselenenylation–selenoxide elimination procedure.[6]

(1) Caine, D.; Kotian, P. L.; McGuiness, M. D. *J. Org. Chem.* **1991**, *56*, 6307.
(2) Ying, B. P.; Yang, P. M.; Zhu, R. H. *Acta. Chim. Sinica* **1987**, *45*, 450; *Chem. Abstr.* **1987**, *107*, 102504n.
(3) Mitsunobu, O. *Synthesis* **1981**, 1.
(4) Micheli, R. A.; Hajos, Z. G.; Cohen, N.; Parrish, D. R.; Portland, L. A.; Sciamanna, W.; Scott, M. A.; Wehrli, P. A. *J. Org. Chem.* **1975**, *97*, 5434.
(5) Stork, G.; Kahne, D. E. *J. Am. Chem. Soc.* **1983**, *105*, 1072.

0022-3263/92/1957-6587$03.00/0