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Chemoenzymatic synthesis of enantiomerically enriched 2-oxobicyclo[*m*.1.0]alkan-3-yl acetate derivatives

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Abstract—Racemic α′-acetoxy α,β-unsaturated cyclopentanone and cyclohexanone have been resolved into the corresponding enantiomerically enriched α′-hydroxylated and acetoxylated compounds with 96–97% ee via PLE hydrolysis. Stereoselectivity in the palladium(II)-catalyzed reaction between the enantiomerically enriched α′-acetoxylated compounds and diazomethane has been investigated. In the α′-acetoxylated cyclopentenone, preferential cyclopropanation occurs in the *anti*-form, whereas α′-acetoxylated cyclohexenone affords both *syn*- and *anti*-products (*syn*:*anti*, 61:36%). The relative configuration of the products was determined by NOE experiments.

1. Introduction

Cyclopropanes are attractive and versatile building blocks for synthetic targets, since the specific reactivity of this carbocyclic ring system[1] renders them useful as synthetic intermediates. Cyclopropane rings are also found in a variety of natural products and biologically active compounds.[2] Consequently, a great deal of effort is devoted to the development of methods, which are aimed at the synthesis of cyclopropanes with high enantioselectivities.[2,3] The transition metal-catalyzed cyclopropanation of olefinic bonds using diazo compounds as a carbene source is among the best developed and most useful methods available to the synthetic organic chemist.[3,4] Alternatively, cyclopropanes can be prepared by addition of trimethyl sulfoxonium iodides to enones.[5]

In particular, cyclopropyl ketones have proven useful as synthetic intermediates.[6] Angle strain and polarization by the carbonyl, impart special reactivity onto these molecules. The most widely applied methods for the synthesis of cyclopropyl ketones include the direct cyclopropanation of α,β-unsaturated ketones[7] and cyclopropanation of allylic alcohols followed by oxidation.[8]

In connection with our work on the development of novel procedures for the direct oxidation of α,β-unsaturated cyclic ketones with $Mn(OAc)_3$[9] in the synthesis of (±)-5-acetoxy-2-cyclopentenone **1a** and (±)-6-acetoxy-2-cyclohexenone **1b** and subsequent PLE catalyzed enzymatic resolution of them into enantiomerically enriched forms,[10] we herein report the results of $Pd(OAc)_2$ catalyzed cyclopropanation with diazomethane.

2. Results and discussion

2.1. Enzymatic hydrolyses of racemic substrates 1a and 1b

The bioconversions of racemic **1a**[9] and **1b**[10] were performed using PLE according to the following procedure, which has already been developed in our group (Scheme 1).[10] To a stirred solution of **1a** or **1b** (500 mg) in a phosphate buffer (pH 7.00, 50 mL), PLE (100 μL) was added in one portion and the reaction mixture stirred at 20 °C in a pH stat unit. The conversions were monitored by TLC. After 5 h, (*S*)-(+)-5-acetoxy-2-cyclopentenone **1a** was obtained with 96% ee in 45% chemical yield (Table 1, entry 1). The bioconversion of substrate **1b** using PLE under the same conditions as above was completed in 3 h. (*S*)-(−)-6-Acetoxy-2-cyclohexenone **1b** was obtained with 97% ee in 46% isolated yield (entry 2). In our previous work,

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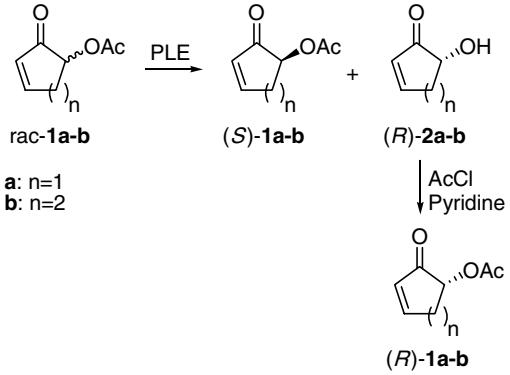
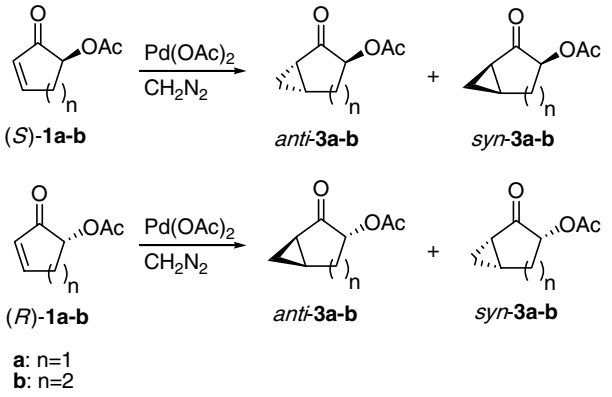


Scheme 1.



Scheme 2.

we showed that 5-hydroxy-2-cyclopentenone **2a** and 6-hydroxy-2-cyclohexenone **2b** could not be isolated in enantiomerically enriched forms due to the racemization and/or rearrangement of α′-hydroxylated cyclic enones as observed in our previous work.[11] In this work, after purification of substrates **2a** and **2b**, they were immediately subjected to acetylation to afford corresponding (*R*)-(−)-5-acetoxy-2-cyclopentenone **1a** and (*R*)-(+)-6-acetoxy-2-cyclohexenone **1b** with 94% ee in 42% chemical yield and 92% ee in 44% chemical yield, respectively (entries 3 and 4).

2.2. Cyclopropanation of substrates (*S*)-(+)-1a, (*R*)-(−)-1a, (*S*)-(−)-1b and (*R*)-(+)-1b

We envisaged the stereoselective synthesis of various 2-oxobicyclo[*m*.1.0]alkan-3-yl acetates using the enantiomerically enriched α′-acetoxy α,β-unsaturated cyclopentenone and cyclohexenone derivatives. Since the palladium-catalyzed cyclopropanation using diazomethane and α,β-unsaturated carbonyl compounds, including cyclopentenones and cyclohexenones, has been used as an efficient method[12], we applied this method to all enantiomerically enriched substrates (*S*)-(+)-**1a**, (*R*)-(−)-**1a**, (*S*)-(−)-**1b** and (*R*)-(+)-**1b** to afford the possible stereoisomers (Scheme 2).

The first cyclopropanation was performed with substrate (*S*)-(+)-**1a** using $Pd(OAc)_2$ and diazomethane prepared in situ according to the following general procedure. To a stirred solution of (*S*)-(+)-**1a** (300 mg, 2.14 mmol) and $Pd(OAc)_2$ (13.32 mg, 0.06 mmol) in ether (30 mL), an ether solution of diazomethane (10 mmol) prepared from *N*-methyl-*N*-nitrosourea was added by distillation and the mixture stirred at 0 °C. The conversion was monitored by TLC. After 4 h, (−)-**3a** was obtained in 98% chemical yield as the single diastereomer, as established by NMR (Table 2, entry 1). The relative configuration of (−)-**3a** was determined by differential NOE experiments. The characteristic methine proton of the acetoxy attached carbon at 5.13 ppm and one of the methylene proton of cyclopropane ring at 1.16–1.25 ppm show significant NOE enhancements, which indicate the *anti*-relationship between the acetoxy group and the cyclopropane moiety. This is presumably the thermodynamically most stable of the possible diastereomers. Thus, the absolute configuration of *anti*-(−)-**3a** was determined as *anti*-(1*S*,3*S*,5*S*)-(−)-**3a**.

The next attempt involved substrate (*S*)-(−)-**1b** using $Pd(OAc)_2$ and diazomethane under the same conditions as above. The chemical yield of the reaction (entry 2) was as high as in the five-membered ring case (97%). In contrast to entry 1, ^{1}H NMR spectra showed the mixture of two diastereomers. The mixture was separated by flash column chromatography to afford (−)-**3b** and (+)-**3b** in 61% and 36% chemical yields, respectively. The configurations of (−)-**3b** and (+)-**3b** were determined by differential NOE experiments. In the differential NOE experiment of (+)-**3b** (as the minor product), we observed significant NOE enhancement between the methine proton of the acetoxy attached carbon at 5.05 ppm and one of the methylene proton of cyclopropane ring at 1.12 ppm and decided that the acetoxy group and the cyclopropane moiety are in an *anti*-relationship. Hence, the configuration of the minor diastereomer *anti*-(+)-**3b** was determined as *anti*-(1*S*,3*S*,6*R*)-(+)-**3b**. In contrast to the minor diastereomer, the major diastereomer (−)-**3b** did not show any NOE enhancement between the characteristic methine proton of acetoxy attached carbon at 4.83 ppm and methylene protons of cyclopropane moiety at 1.05–1.11 and 1.15–1.19 ppm. The configuration of *syn*-(−)-**3b** was determined as *syn*-(1*R*,3*S*,6*S*)-(−)-**3b**.

Table 1.

Entry	Substrate	Time (h)	Acetoxy product	Yield (%)[a]	$[\alpha]_D^{20}$	ee (%)[b]
1	(±)-**1a**	5	(*S*)-(+)-**1a**	45	+60.3	96
2	(±)-**1b**	3	(*S*)-(−)-**1b**	46	−88.7	97
3	(−)-**2a**	—	(*R*)-(−)-**1a**	42	−59.1	94
4	(+)-**2b**	—	(*R*)-(+)-**1b**	44	+84.2	92

[a] Yields (%) are given as the isolated yields. In entries 3 and 4, yields (%) are calculated with respect to corresponding racemic substrates.
[b] Enantiomeric excess values are determined using Chiralcel ODH chiral column HPLC analysis.

Table 2.

Entry	Substrate	Time (h)	*syn*-Product	Yield (%)	$[\alpha]_D^{20}$	*anti*-Product	Yield (%)	$[\alpha]_D^{20}$
1	(*S*)-(+)-**1a**	4	—	—	—	(1*S*,3*S*,5*S*)-(−)-**3a**	98	−22.0
2	(*S*)-(−)-**1b**	3	(1*R*,3*S*,6*S*)-(−)-**3b**	61	−22.05	(1*S*,3*S*,6*R*)-(+)-**3b**	36	+5.0
3	(*R*)-(−)-**1a**	4	—	—	—	(1*R*,3*R*,5*R*)-(+)-**3a**	97	+21.3
4	(*R*)-(+)-**1b**	3	(1*S*,3*R*,6*R*)-(+)-**3b**	63	+20.52	(1*R*,3*R*,6*S*)-(−)-**3b**	34	−4.2

In entry 3, (*R*)-(−)-5-acetoxy-2-cyclopentenone **1a** was also subjected to cyclopropanation under the same conditions as above to confirm the yield and absolute configuration assignment of the resultant oppositely configured product. Comparison of the specific rotation value of the product with (−)-**3a** showed an opposite sign, which proves the enantiomeric relationship. In entry 4, a similar comparison was carried out by the cyclopropanation products of (*R*)-(+)-**1b** with the results obtained in entry 2. We observed the enantiomeric relationships between the pairs of the products in entries 2 and 4.

3. Conclusion

Herein, we have improved the direct stereoselective cyclopropanations of enantiomerically enriched α′-acetoxy α,β-unsaturated cyclopentane (*S*)-(+)-**1a** and cyclohexane (*S*)-(−)-**1b**, respectively, using $Pd(OAc)_2$ and diazomethane in good yields, and have shown that five-membered ring enone (*S*)-(+)-**1a** afforded only *anti*-diastereomers (1*S*,3*S*,5*S*)-(−)-**3a** whereas the six-membered enone (*S*)-(−)-**1b** afforded the both the *syn*- and *anti*-diastereomer (1*R*,3*S*,6*S*)-(−)-**3b** and (1*S*,3*S*,6*R*)-(+)-**3b** as the major and minor products, respectively. The configurations of *anti*-(−)-**3a**, *syn*-(−)-**3b** and *anti*-(+)-**3b** were determined by differential NOE experiments. The enantiomers (*R*)-(−)-**1a** and (*R*)-(+)-**1b** were also subjected to the palladium-catalyzed cyclopropanation reactions and the findings confirmed the results obtained in the first set of experiments.

4. Experimental

The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker Spectrospin Avance DPX 400 spectrometer. Chemical shifts are given in parts per million downfield from tetramethylsilane. Apparent splittings are given in all cases. Infrared spectra were obtained from KBr pellets on a Mattson 1000 FT-IR spectrophotometer. Mass spectra were recorded on a Varian MAT 212. Optical rotations were measured in a 1 dm cell using a Rudolph Research Analytical Autopol III polarimeter at 20 °C. HPLC measurements were performed with ThermoFinnigan Spectra System instrument. Separations were carried out on Chiralcel OD-H analytical column (250 × 4.60 mm) with hexane/2-propyl alcohol as eluent. Column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2-mm silica gel 60 F_{254} analytical aluminium plates. PLE (Pig Liver Esterase) was purchased from Sigma as a suspension in ammonium sulfate solution (3.2 mol/L).

4.1. General procedure for enzymatic hydrolyses of (±)-1a and 1b

To a stirred solution of 500 mg *rac*-**1a**,**1b** in 50 mL of pH 7.00 phosphate buffer, 100 μL PLE was added in one portion and the reaction mixture stirred at 20 °C in a pH stat unit. The conversion was monitored by TLC. The reaction mixture was extracted with ethyl acetate, dried over $MgSO_4$ and concentrated under reduced pressure. The product was purified by flash column chromatography (EtOAc–hexane, 1:3). Compounds (*S*)-(+)-**1a** and (*S*)-(−)-**1b** were isolated and are in accordance with the literature data.[10] The isolated products (*R*)-**2a** and (*R*)-**2b** were directly subjected to an acetylation reaction to prevent their complete racemization. To a stirred solution of (*R*)-**2a**,**2b** (250 mg, 2.55 and 2.23 mmol, respectively) in CH_2Cl_2 (10 mL), dry pyridine (300 mg, 3.75 mmol) was added at 0 °C and stirred for 30 min. Acetylchloride (300 mg, 3.75 mmol) was then added dropwise. The resultant mixture was stirred for 12 h at room temperature. The organic phase was extracted with 0.1 M HCl (3 × 10 mL), saturated $NaHCO_3$ (3 × 10 mL) and brine (2 × 10 mL), dried over $MgSO_4$ and solvent was evaporated under reduced pressure to afford quantitatively (*R*)-(−)-**1a** and (*R*)-(+)-**1b**. All are in accordance with the literature data.[10]

4.1.1. (*S*)-(+)-5-Acetoxy-2-cyclopentenone (*S*)-(+)-1a. (0.23 g, 45%) as a colourless oil; 96% ee $[\alpha]_D^{20} = +60.3$ (*c* 0.2, $CHCl_3$).

4.1.2. (*S*)-(−)-6-Acetoxy-2-cyclohexenone (*S*)-(−)-1b. (0.23 g, 46%) as a colourless oil; 97% ee $[\alpha]_D^{20} = -88.7$ (*c* 0.5, MeOH).

4.1.3. (*R*)-(−)-5-Acetoxy-2-cyclopentenone (*R*)-(−)-1a. (0.25 g, 49%) as a colourless oil; 94% ee $[\alpha]_D^{20} = -59.1$ (*c* 0.2, $CHCl_3$).

4.1.4. (*R*)-(+)-6-Acetoxy-2-cyclohexenone (*R*)-(+)-1b. (0.22 g, 44%) as a colourless oil; 92% ee $[\alpha]_D^{20} = +84.2$ (*c* 0.5, MeOH).

4.2. General procedure for cyclopropanation of (*S*)-(+)-1a, (*S*)-(−)-1b, (*R*)-(−)-1a and (*R*)-(+)-1b

$Pd(OAc)_2$ (13.32 mg, 0.059 mmol) was added to an ice-cooled solution of substrate (*S*)-**1a**,**1b** or (*R*)-**1a**,**1b** (300 mg, 2.14 mmol) in ether (30 mL). To this solution, an etheral solution of diazomethane prepared from *N*-methyl-*N*-nitrosourea (720 mg, 10.0 mmol) and KOH (2.0 g, 35.6 mmol) was distilled. The resultant mixture was stirred at 0 °C for 4 h. The conversion was monitored by TLC. The reaction mixture was allowed to warm to room temperature and then filtered through a

pad of Celite and concentrated. The product was purified by flash column chromatography (EtOAc–hexane 1:3).

4.2.1. (1*S*,3*S*,5*S*)-(−)-2-Oxobicyclo[3.1.0]hexan-3-yl acetate *anti*-(1*S*,3*S*,5*S*)-(−)-3a. (294 mg, 98%) as a colourless oil; 96% ee $[\alpha]_D^{20} = -22.0$ (*c* 0.2, $CHCl_3$); ν_{max} (neat) 2989, 2956, 2925, 1732, 1639 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.12 (1H, t, $J = 8.4$ Hz, C*H*OAc), 2.58 (1H, ddd, $J = 12.5$, 8.1, 4.4 Hz, CH_aH_bCHOAc), 2.13 (3H, s, *Me*CO_2), 2.05–2.16 (2H, m, CH_aH_bCHOAc and cyclopropylC*H*CO), 1.89–1.92 (1H, m, cyclopropylC*H*CHCO), 1.26–1.29 (1H, m, cyclopropylCH_{exo}-H_{endo}), 1.16–1.19 (1H, m, cyclopropylC$H_{exo}H_{endo}$); δ_C (100.6 MHz, $CDCl_3$) 207.6, 170.5, 70.9, 29.2, 24.9, 21.0, 20.3, 15.2; HRMS (EI): M+, found 154.0629, $C_8H_{10}O_3$ requires 154.0630.

4.2.2. (1*R*,3*R*,5*R*)-(+)-2-Oxobicyclo[3.1.0]hexan-3-yl acetate *anti*-(1*R*,3*R*,5*R*)-(+)-3a. (320 mg, 97%) as a colourless oil; 94% ee $[\alpha]_D^{20} = +21.3$ (*c* 0.2, $CHCl_3$).

4.2.3. (1*R*,3*S*,6*S*)-(−)-2-Oxobicyclo[4.1.0]heptan-3-yl acetate *syn*-(1*R*,3*S*,6*S*)-(−)-3b. (199 mg, 61%) as a colourless oil; 97% ee $[\alpha]_D^{20} = -22.05$ (*c* 0.2, $CHCl_3$); ν_{max} (neat) 2980, 2952, 2870, 1746, 1712 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.83 (1H, dd, $J = 13.0$, 6.4 Hz, C*H*OAc), 2.13–2.20 (2H, m, CH_2CH_2CHOAc), 2.11 (3H, s, *Me*CO_2), 1.82–1.88 (1H, m, CH_aH_bCHOAc), 1.70–1.79 (2H, m, CH_aH_bCHOAc and cyclopropylC*H*CO), 1.59–1.69 (1H, m, cyclopropylC*H*CHCO), 1.16 (1H, q, $J = 5.5$ Hz, cyclopropylCH_aH_b), 1.05–1.11 (1H, m, cyclopropylCH_aH_b); δ_C (100.6 MHz, $CDCl_3$) 202.3, 170.3, 74.2, 24.4, 21.6, 21.3, 21.0, 15.0, 8.9; HRMS (EI): M+, found 168.0783, $C_9H_{12}O_3$ requires 168.0786.

4.2.4. (1*S*,3*R*,6*R*)-(+)-2-Oxobicyclo[4.1.0]heptan-3-yl acetate *syn*-(1*S*,3*R*,6*R*)-(+)-3b. (206 mg, 63%) as a colourless oil; 92% ee $[\alpha]_D^{20} = +20.5$ (*c* 0.2, $CHCl_3$).

4.2.5. (1*S*,3*S*,6*R*)-(+)-2-Oxobicyclo[4.1.0]heptan-3-yl acetate *anti*-(1*S*,3*S*,6*R*)-(+)-3b. (118 mg, 36%) as a colourless oil; 97% ee $[\alpha]_D^{20} = +5.0$ (*c* 0.2, $CHCl_3$); ν_{max} (neat) 2985, 2946, 2886, 2853, 1754, 1720 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.05 (1H, dd, $J = 11.0$, 5.5 Hz, C*H*OAc), 2.15–2.29 (2H, m, CH_2CH_2CHOAc), 2.14 (3H, s, *Me*CO_2), 1.98–2.06 (1H, m, CH_aH_bCHOAc), 1.88–1.96 (2H, m, CH_aH_bCHOAc and cyclopropylC*H*CO), 1.78–1.94 (1H, m, cyclopropylC*H*CHCO), 1.32–1.38 (1H, m, cyclopropylC$H_{exo}H_{endo}$), 1.11 (1H, q, $J = 5.5$ Hz, cyclopropylC$H_{exo}H_{endo}$); δ_C (100.6 MHz, $CDCl_3$) 203.2, 170.3, 72.1, 32.2, 26.4, 22.0, 21.2, 21.0, 18.4; HRMS (EI): M+, found 168.0784, $C_9H_{12}O_3$ requires 168.0786.

4.2.6. (1*R*,3*R*,6*S*)-(−)-2-Oxobicyclo[4.1.0]heptan-3-yl acetate *anti*-(1*R*,3*R*,6*S*)-(−)-3b. (110 mg, 34%) as a colourless oil; 92% ee $[\alpha]_D^{20} = -4.2$ (*c* 0.2, $CHCl_3$).

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