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Lipase-catalyzed selective benzoylation of 1,2-diols with vinyl benzoate in organic solvents

Pierangela Ciuffreda, Laura Alessandrini, Giancarlo Terraneo and Enzo Santaniello*

Dipartimento di Scienze Precliniche LITA Vialba-Università degli Studi di Milano, Via G. B. Grassi, 74-20157 Milano, Italy

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Abstract—Lipases from *Mucor miehei* (MML) and *Candida antarctica* (CAL) are able to catalyze the benzoylation of the primary hydroxy group of 1,2-diols with vinyl benzoate in organic solvents. We have studied the MML-catalyzed benzoylation that proceeds with high regioselectivity and moderate enantioselectivity, whereas in the dibenzoylation reaction activity of MML and stereoselectivity of the enzymatic process is strongly influenced by steric factors.

1. Introduction

Ester synthesis via acyl transfer reactions can be efficiently catalyzed by lipases in organic solvents and the application of this biocatalytic approach to organic synthesis has been extensively reviewed.[1–4] One of the most effective transesterification procedures relies upon the irreversible reaction originally developed for vinyl or propenyl esters as acylating reagents,[5,6] a method that has enjoyed widespread application in organic synthesis.[7–9] Vinyl acetate (VA) is by far the enol ester most used in this reaction, although many reports have pointed out the influence of the structure of the acyl donor on the activity and selectivity of the enzyme.[10–12] Considering an ester as an alcohol protecting group, benzoate should be more resistant than acetate and, therefore, more useful for applications in organic synthesis, especially if applied to polyhydroxylated compounds for which the regio- and enantioselective control of protection procedures is highly desirable. Furthermore, a benzoate should be less prone to migration towards a vicinal hydroxy group, a reaction that frequently occurs for acetyl moieties,[13] specially in the case of 1,2-diols. It should finally be remembered that, in general, the selective protection of diols by chemical methods is often difficult to achieve or requires special reagents and experimental conditions. For instance, the selective benzoylation of the primary hydroxy group of 1,2-diols can be obtained only by a few methods, including microwave heating.[14] On the basis of the above premises, we have investigated the enzymatic benzoylation of 1,2-diols that could be catalyzed by a suitable lipase in an organic solvent using as acyl transfer vinyl benzoate (VB), a commercially available vinyl ester occasionally used for lipase-catalyzed benzoylations.[15–17]

2. Results and discussion

2.1. Lipase-catalyzed benzoylation of propane-1,2-diol 1a

We selected propane-1,2-diol **1a** as a model substrate to set up experimental conditions such as, choice of the most suitable lipase, the proper organic solvent and the lipase/substrate ratio. We focused on lipases that have been most widely used for synthetic applications of the transesterification with VA.[18] Microbial lipases from *Pseudomonas cepacia* (PCL), *Muchor miehei* (MML), *Candida antarctica* (CAL), *Candida cylindracea* (or *C. rugosa*, CCL) and the porcine pancreas lipase (pPL) were selected as biocatalysts. It should be remembered that some lipases are available as partially purified native proteins (PCL, CCL, pPL) whereas CAL and MML are also available in an immobilized form. There are no rules to establish the amount of the enzyme to be used in organic solvents and, therefore, we used 0.1 g of the enzymatic preparation per millimole of **1a**, independently from the hydrolytic activity of the lipase. The time limit of the reaction was arbitrarily fixed in 72 h and *tert*-butyl methyl ether (*t*BuOMe) was selected as

* Corresponding author. Tel.: +390250319691; fax: +390250319631; e-mail: enzo.santaniello@unimi.it

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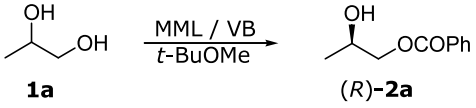
the solvent, on the basis of our recent report on the enzymatic benzoylation to 1,4-diols.[19] We have also established that no benzoylation occurred in the absence of lipase.

The results of the enzymatic benzoylation of **1a** with all previously selected lipases are shown in Table 1. CAL and MML are able to catalyze the regioselective acylation to the 1-benzoate **2a** (Scheme 1) much faster than other enzymes, MML being the most active biocatalyst. The monobenzoate **2a** did not show any propensity to migrate during the purification on silica gel chromatography and could be stored at room temperature with unlimited stability. ^{1}H NMR analysis of the ester obtained by reaction of **2a** with (*S*)-α-methoxy-α-(trifluoromethyl)-phenyl chloride [(*S*)-MTPACl][20] indicated 61% enantiomeric excess (ee) at 30% conversion of **1a** to the monobenzoate **2a** that corresponds to an enantiomeric ratio *E* of 5.3.[21] The (*R*)-configuration was assigned to the enzymatically prepared monobenzoate **2a** by analysis of the ^{1}H NMR data of the (*R*)- and (*S*)-MTPA esters of **2a**, according to the modified Mosher's method.[22] In fact, the chemical shifts of protons at position 1 of (*R*)-MTPA ester appear significantly shielded with respect to those of the (*S*)-MTPA diastereomer (+42 Hz for proton **1a**, +24 Hz for proton **1b**). On the other hand, the chemical shifts of methyl protons at position 3 appear deshielded in (*R*)-MTPA ester relative to (*S*)-MTPA one (−18 Hz). Finally, the assignment was confirmed by comparison of the specific rotation of our sample with the value reported in the literature.[23]



Scheme 1.

Table 1. Lipase-catalyzed benzoylation of propane-1,2-diol **1a**

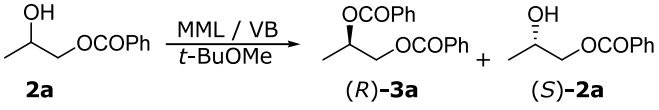
Lipase[a]	Convn (%)	Time (h)	Ee (%)	*E*
MML	100	1	–	–
MML	30	0.10	61[b]	5.3
MML	60	0.25	70[c]	5.5
CAL	100	4.5	–	–
CAL	37	1.5	54[b]	4.5
CAL	63	2.1	64[c]	4.6
PCL	52	72	–	–
CCL	21	72	–	–
pPL	33	72	–	–

[a] 100 mg enzyme/mmol substrate.
[b] Determined by ^{1}H NMR analysis of MTPA esters of monobenzoate **2a**.
[c] Determined by ^{1}H NMR analysis of MTPA esters of unreacted **1a**.

The reaction with CAL was also examined, but no improvement of the enantioselectivity was observed.

2.2. Lipase-catalyzed benzoylation of 2-hydroxypropyl benzoate 2a

It should be mentioned that, in general, the lipase-catalyzed monoacetylation of racemic 1,2-diols fails to provide a stereoselective resolution,[24] but this can be successfully achieved only by converting the diol to the corresponding diacetate. By this 'sequential acetylation', enantiomerically pure diacetate or unreacted diol can be finally obtained.[25] We considered that, by analogy with the enzymatic acetylation, the enantioselectivity of the lipase-catalyzed benzoylation could be enhanced by converting the racemic monobenzoate **2a** to the dibenzoate **3a** (Scheme 2). The dibenzoylation was slow (62% in 40 h) and proceeded with an *E* value of 9.2 that corresponds to an improvement of enantioselectivity if compared to the monobenzoylation of diol **1a** (*E* 5.3). Application of modified Mosher's method and measurement of the optical rotation established (*S*)-configuration for unreacted monobenzoate **2a**. Therefore, the stereochemical outcome of the second benzoylation was such that starting from (*R*,*S*)-monobenzoate **2a** the (*R*)-enantiomer was converted into (*R*)-dibenzoate **3a.** Finally, the above obtained *E* value 9.2 can be considered just acceptable for asymmetric synthesis and we decided to study in more detail the dependence of the enantioselectivity on the nature of the solvent[26] (Table 2).



Scheme 2.

Table 2. MML-catalyzed benzoylation of monobenzoate **2a** in different solvents

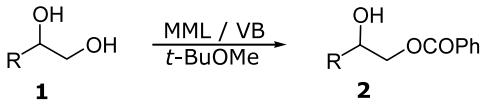
Solvent	Convn (%)	Time (h)	Ee[a] (%)	*E*
Hexane	61	4	85	8.7
Toluene	63	29	82	6.9
t-BuOMe	62	40	88	9.2
$CHCl_3$	17	168	–	–
THF	26	168	–	–

[a] Determined by ^{1}H NMR analysis of MTPA esters of unreacted monobenzoate **2a**.

The reaction was faster in apolar solvents such as hexane or toluene, but no improvement of *E* could be achieved. In polar solvents such as $CHCl_3$ or THF the reaction was considerably slower and the enantioselectivity was not further examined.

2.3. Mono- and dibenzoylation of 1,2-diols 1b–f

We extended the above preliminary observations to a few additional diols (Scheme 3) that contained aliphatic **1b**,**c** and aromatic residues **1d**,**e**, as well as a double bond near to the secondary hydroxy group **1f**.



1 **2**

a: R = CH_3 **b**: R = C_4H_9 **c**: R = C_8H_{17}
d: R = Ph **e**: R = CH_2Ph **f**: R = $CH{=}CH_2$

Scheme 3.

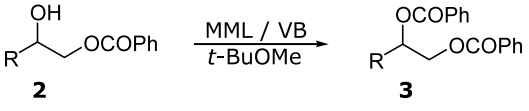
For all substrates we examined only the MML-catalyzed benzoylation in *t*-BuOMe that proceeded to quantitative conversion in 1–5 h (Table 3).

Table 3. MML-catalyzed benzoylation of diols **1b–f** in *t*-BuOMe

Substrate	Convn (%)	Time (h)	Ee (%)	*E*
1b	100	2	–	–
1b	72	0.5	31[a]	1.6
1c	100	2	–	–
1c	70	0.5	30[a]	1.7
1d	100	3	–	–
1d	36	0.25	51[b]	4.0
1e	100	5	–	–
1e	39	1.1	15[b]	1.5
1f	100	1	–	–
1f	23	0.4	27[b]	1.9

[a] Determined by ^{1}H NMR analysis of MTPA esters of unreacted diols.
[b] Determined by ^{1}H NMR analysis of MTPA esters of monobenzoates.

Interestingly, the unsaturated diol **1f** reacted as fast as **1a**, whereas no significant differences could be observed between diols of different structural frameworks such as **1b–e**. The enzymatic reaction proceeded with complete regioselectivity, but the enantioselectivity was only modest (*E* 1.6–4.0). For all monobenzoates **2b–f** ^{1}H NMR analysis allowed the (*R*)-configuration to be established. Enzymatic preparation of dibenzoates **3b–f** (Scheme 4) by VB-mediated benzoylation of monobenzoates **2b–f** proceeded at a slow conversion rate (Table 4). Significantly, only monobenzoate **2f** reacted as fast as **2a** suggesting that steric factors may play an important role in the dibenzoylation reaction. The significant enantioselectivity that had been obtained in the conversion of monobenzoate **2a** to **3a** could not be observed in all other cases, the *E* value not exceeding 2.8 and the stereochemical outcome of the reaction was not investigated.



2 **3**

a: R = CH_3 **b**: R = C_4H_9 **c**: R = C_8H_{17}
d: R = Ph **e**: R = CH_2Ph **f**: R = $CH{=}CH_2$

Scheme 4.

Table 4. MML-catalyzed benzoylation of monobenzoates **2a–f** in *t*-BuOMe

Substrate	Convn (%)	Time (days)	Ee[a] (%)	*E*
2a	65	2	88	9.2
2b	66	5	52	2.7
2c	60	5	38	2.3
2d	64	7	26	1.7
2e	62	20	40	2.3
2f	64	2	50	2.8

[a] Determined by ^{1}H NMR analysis of MTPA esters of unreacted monobenzoate **2a**.

3. Conclusions

We have shown that, among selected enzymes, CAL and MML are suitable to carry on the benzoylation of 1,2-diols at a rate that can be compatible with preparative applications. The enantioselectivity of the monobenzoylation is appreciable mainly for propane-1,2-diol **1a** and the stereoselection is enhanced by further benzoylation only in the case of monobenzoate **2a**. Improved enantioselectivity was not observed for other substrates **2b–2f**. Presumably the steric constrictions related to the presence of the benzoylated primary group in the substrate of the enzymatic reaction determine also long time for conversion (2–20 days). These limiting factors of the dibenzoylation reaction are transformed into a clear advantage, if regioselectivity is considered. In fact, under the selected conditions, the efficient benzoylation of 1,2-diols catalyzed by CAL and MML proceeds with an absolute regioselectivity to the corresponding 1-benzoates. Further studies are required to investigate in more detail these enzymatic reactions and to answer to the questions raised by the results so far obtained in the present research.

4. Experimental

4.1. General

Optical rotations were measured on a Perkin–Elmer 241 polarimeter (sodium D line at 25°C). Melting points were obtained using a Stuart Scientific SMP3 instrument and are uncorrected. ^{1}H NMR spectra were recorded on Bruker AM-500 spectrometer operating at 500.13 MHz and are referenced to residual $CHCl_3$ proton of the solvent $CDCl_3$ at 7.24 ppm; coupling constants (*J*) are given in hertz. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F_{254} precoated plates with a fluorescent indicator. Flash chromatography[27] was performed using Merck silica gel 60 (230–400 mesh) using appropriate mixtures of hexane and ethyl acetate as eluants. GLC analyses were carried out on a SPB-5 Supelco column (30 m×0.32 mm; 0.25 mm ID, film thickness 0.25 μm). (*R*)-MTPA derivatives were prepared from the appropriate (*S*)-MTPA chlorides. The progress of all reactions, column chromatography and compound purity were monitored by TLC, GLC and/or HPLC. All reagents were obtained from commercial sources and used without further purification.

Porcine pancreas lipase (24 U/mg solid) was purchased from Fluka. Lipase from *Pseudomonas* sp. (Lipase PS 'Amano', 30 U/mg solid) and from *Candida cylindracea* (Lipase AYS 'Amano', 31.6 U/mg solid) were purchased from Amano Pharmaceutical. *Candida antarctica* lipase (Novozym 435®, acrylic resin supported lipase, 11.4 U/mg solid) was a generous gift of Novo Nordisk Bioindustrial Group. Lipase from *Mucor miehei* (Chirazyme® L-9, c.-f., C2, lyo, carrier-fixed lipase, 8 U/mg solid) was purchased from Roche Diagnostics GmbH.

Diols **1a**–**d** and **1f** were commercially available. Diol **1e** was prepared by lithium aluminum hydride reduction of methyl phenyllactate.

4.2. Lipase-mediated benzoylation of propane-1,2-diol 1a

Propane-1,2-diol (76 mg, 1.0 mmol), VB (3.0 mmol) and lipase (100 mg) were suspended in solvent (10 ml). The mixture was allowed to react at rt and the progress of the reaction monitored by TLC and GLC. When the reaction was complete, the enzyme was filtered off and washed with MeOH, the solvents were distilled under vacuum and the product was purified by flash chromatography. Elution with hexane/AcOEt (8:2) afforded pure compound **2a** as a colorless oil (173 mg, 96% for the MML catalyzed reaction at 100% conversion). At 30% conversion, purified (*R*)-**2a** was obtained in 28% yield; $[\alpha]_D^{25}$ −12.9 (*c* 1, $CHCl_3$); lit.:[23] $[\alpha]_D^{25}$ +21.8 (*c* 1, $CHCl_3$) for enantiomerically pure (*S*)-**2a**; ^{1}H NMR ($CDCl_3$) δ 8.04 (2H, d, J=7.0 Hz, H-2′ and H-6′), 7.54 (1H, t, J=7.0 Hz, H-4′), 7.41 (2H, dd, J=7.0 and 7.0 Hz, H-3′ and H-5′), 4.30 (1H, ddq, J=4.2, 5.6 and 6.3 Hz, H-2), 4.21-4.16 (2H, m, part AB of system ABX, H-1a and H-1b), 1.27 (3H, d, J=5.6 Hz, CH_3).

4.3. Lipase-mediated benzoylation of diols 1b–f

The experimental protocol was as described for **1a** using a 100 mg/mmol enzyme/substrate ratio. At 100% conversion, 96–98% yield of monobenzoates **2b**–**f** were isolated after flash chromatography using hexane/AcOEt (90:10) as eluant. ^{1}H NMR spectra of isolated and purified monobenzoates **2b**–**f** are described in details.

4.3.1. 2-Hydroxyhexyl benzoate 2b.[28] ^{1}H NMR δ 8.04 (2H, d, J=7.0 Hz, H-2′ and H-6′), 7.55 (1H, t, J=7.0 Hz, H-4′), 7.44 (2H, dd, J=7.0 and 7.0 Hz, H-3′ and H-5′), 4.39 (1H, dd, J=3.5 and 11.2 Hz, H-1a), 4.21 (1H, dd, J=7.0 and 11.2 Hz, H-1b), 3.97 (1H, ddt, J=3.5, 7.0 and 7.0 Hz, H-2), 1.59–1.54 (2H, m, H-3a and H-3b), 1.39–1.31 (4H, m, CH_2-4, CH_2-5) and 0.91 (3H, t, J=7.0 Hz, CH_3-6).

4.3.2. 2-Hydroxydecyl benzoate 2c.[14] ^{1}H NMR δ 8.04 (2H, d, J=7.0 Hz, H-2′ and H-6′), 7.55 (1H, t, J=7.0 Hz, H-4′), 7.43 (2H, dd, J=7.0 and 7.0 Hz, H-3′ and H-5′), 4.36 (1H, dd, J=3.5 and 11.2 Hz, H-1a), 4.21 (1H, dd, J=7.0 and 11.2 Hz, H-1b), 3.97 (1H, ddt, J=3.5, 7.0 and 7.0 Hz, H-2), 1.57–1.50 (2H, m, H-3a, H-3b), 1.33–1.23 (12H, m, CH_2 X 6) and 0.86 (3H, t, J=7.0 Hz, CH_3-6).

4.3.3. 2-Hydroxy-2-phenylethyl benzoate 2d.[29] Mp 65–67°C; ^{1}H NMR δ: 8.08 (2H, d, J=7.0 Hz, H-2′ and H-6′), 8.04 (2H, d, J=7.0 Hz, H-2″ and H-6″), 7.60 (1H, t, J=7.0 Hz, H-4″), 7.56 (1H, t, J=7.0 Hz, H-4′), 7.46 (2H, dd, J=7.0 and 7.0 Hz, H-3′ and H-5′), 7.38 (2H, dd, J=7.0 and 7.0 Hz, H-3″ and H-5″), 5.12 (1H, dd, J=3.5 and 8.4 Hz, H-2), 4.52 (1H, dd, J=3.5 and 11.2 Hz, H-1a) and 4.42 (1H, dd, J=8.4 and 11.2 Hz, H-1b).

4.3.4. 2-Hydroxy-2-phenylpropyl benzoate 2e. Colorless oil, ^{1}H NMR δ 8.04 (2H, d, J=7.0 Hz, H-2″ and H-6″), 7.55 (1H, t, J=7.0 Hz, H-4″), 7.43 (2H, dd, J=7.0 and 7.0 Hz, H-3″ and H-5″), 7.31 (2H, dd, J=7.0 and 7.0 Hz, H-3′ and H-5′), 7.24 (2H, d, J=7.0 Hz, H-2′ and H-6′), 7.23 (2H, t, J=7.0 Hz, H-4′), 4.41 (1H, dd, J=3.5 and 11.2 Hz, H-1a), 4.27 (1H, dd, J=7.0 and 11.2 Hz, H-1b), 4.22 (1H, dddd, J=3.5, 5.6, 7.0 and 7.0 Hz, H-2), 2.93 (1H, dd, J=5.6 and 13.3 Hz, H-3a), 2.87 (1H, dd, J=7.0 and 13.3 Hz, H-3b). Found: C, 73.30; H, 9.44. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41%.

4.3.5. 2-Hydroxybut-3-en benzoate 2f.[30] ^{1}H NMR δ 8.03 (2H, d, J=7.0 Hz, H-2′ and H-6′), 7.56 (1H, t, J=7.0 Hz, H-4′), 7.43 (2H, dd, J=7.0 and 7.0 Hz, H-3′ and H-5′), 5.93 (1H, ddd, J=5.6, 10.5 and 16.8 Hz, H-3), 5.43 (1H, dd, J=1.4 and 16.8 Hz, H-4a), 5.27 (1H, dd, J=1.4 and 10.5 Hz, H-4b), 4.52 (1H, ddd, J=3.5, 5.6 and 7.0 Hz, H-2), 4.41 (1H, dd, J=3.5 and 11.2 Hz, H-1a), 4.28 (1H, dd, J=7.0 and 11.2 Hz, H-1b).

4.4. MML catalyzed benzoylation of monobenzoates 2b–f

The reaction was carried out following the same protocol of monobenzoylation. The dibenzoates **3a**–**f** showed spectroscopic data in accord with the structure.

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