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Practical one-pot sequence for the asymmetric synthesis of 1,2 diols from primary alcohols

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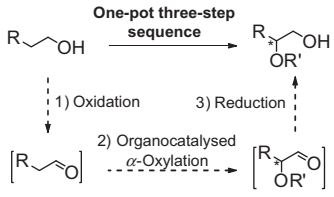
ABSTRACT

A practical one-pot three-step sequence is reported for the asymmetric synthesis of α-benzoyloxylated alcohols from primary alcohols. Good overall yields (36–52%) and enantioselectivities (91–94% e.e.) are obtained using a commercial organocatalyst in the key oxylation reaction. A simple modification in the protocol allows the formation of enantioenriched γ-benzoyloxylated α,β-unsaturated ester from alcohol. Synthetic utility has been harnessed to the easy preparation of (−)-γ-octalactone from hexan-1-ol.

Organocatalytic one-pot reactions have attracted much attention in the actual context of 'Green Chemistry', by avoiding both purification procedures and metallic chemicals.[1] This strategy has become a new powerful tool for multi-step and total syntheses, allowing rapid and stereoselective access to complex structures from simple starting materials.[2] The structural diversity is often created from carbonyl compounds by an enamine or iminium activation step, which is followed by the asymmetric addition of various electrophiles or nucleophiles. Aldehydes proved to be particularly versatile precursors in these processes but are known to be sensitive to storage and to degrade in time. Thus, their formation in situ prior to an organocatalysed functionalisation would be highly desirable.[3] Two strategies have been recently described for such combination, both starting from stable alcohols. Alexakis and Mazet reported the one-pot isomerisation of allylic alcohols to aldehydes catalysed by an iridium complex and their following organocatalysed α-functionalisation.[4] Rueping et al. described a ruthenium-based oxidative system to generate aldehydes which were further involved in a series of organocatalysed transformations.[5] However, only propargylic and allylic alcohols were compatible for this oxidation strategy.

In line with our interests on the organocatalysed asymmetric α-functionalisation of carbonyl compounds,[6] we aimed to develop the direct synthesis of monoprotected 1,2-diols from primary alcohols. A one-pot three-step sequence was proposed, composed of an oxidation, an α-oxylation and a subsequent reduction (Scheme 1).

The key step, consisting in the organocatalysed α-oxylation of aldehydes, led to the creation of the chiral centre.[7] From the various oxygen donors described for this reaction, we identified the readily available and inexpensive benzoylperoxide[8] (BPO) as a suitable reagent. Recently Hayashi showed that a catalytic amount of diphenylprolinol *tert*-butyldimethylsilyl ether (20 mol %) allowed the benzoyloxylation of aldehydes with yield up to 78%.[8c] Maruoka described also the benzoyloxylation of aldehydes in the presence of radical scavengers using 2-tritylpyrrolidine (10 mol %). Indeed, the α-acylation of 3-phenylpropanal led to the product with a yield of 52% by adding 10 mol % of 2,2,6,6-tetramethyl-1-piperidinyl-oxyl (TEMPO).[8a] In our sequence, the choice of the oxidation conditions in the first step was critical as by-products needed to be fully compatible with the following steps. Catalytic TEMPO in the presence of the iodine(III) co-oxidant [bis(acetoxy)iodo]benzene (BAIB) in dichloromethane was selected. This system is known for smooth conversion of primary alcohols into aldehydes,[9] and minimal impact was expected from co-produced acetic acid and iodobenzene on the subsequent steps. We assumed that the benzoyloxylation



Scheme 1. One-pot strategy for asymmetric synthesis of monoprotected 1,2-diols from primary alcohols.

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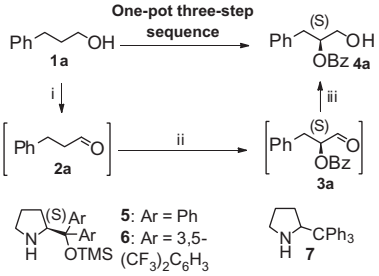
Table 1
Optimisation of the oxidation/α-benzoyloxylation/reduction sequence



Entry	Solvent	BPO (equiv)	Cat.	Yield[a] (%)	e.e.[b] (%)
1	CH_2Cl_2	1.5	(*S*)-**5**	49	91
2	THF	1.5	(*S*)-**5**	52	94
3[c]	THF	1.5	(*S*)-**5**	50	94
4	THF	1.5	(*S*)-**6**	40	92
5	THF	1.1	(*S*)-**5**	52	94
6[d]	THF	1.1	(*S*)-**5**	52	94
7	THF	1.1	(±)-**7**	57	0

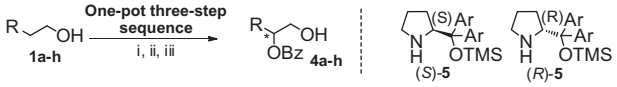
Reagents and conditions: (i) $PhI(OAc)_2$ (1.0 equiv, 0.25 mmol), TEMPO (10 mol %), **1a** (1.1 equiv) in solvent (1 mL), rt, 16 h; (ii) BPO (*n* equiv), Catalyst (10 mol %) in THF (1 mL), rt, 5 h; (iii) $NaBH_4$ (4 equiv), rt, 16 h.
[a] Purified yield.
[b] Determined by HPLC analysis.
[c] 1.0 equiv of **1a**.
[d] 20 mol % of (*S*)-**5**.

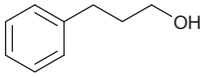
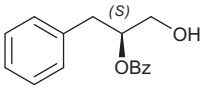
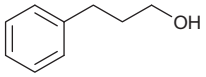
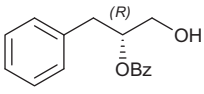
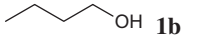
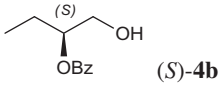
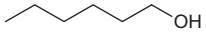
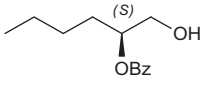
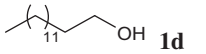
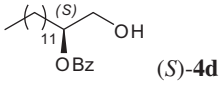
reaction could be done in the presence of TEMPO introduced in the previous oxidation step. A slight excess of alcohol (1.1 equiv) has been used to ensure full consumption of $PhI(OAc)_2$ after the first reaction. Furthermore, an in situ reduction by $NaBH_4$ was envisaged, to afford directly the desired and stable monoprotected 1,2-diol at the end of the sequential addition. This simple three-step procedure would fully satisfy the desired criteria: avoiding work-up and purification of any aldehyde intermediates, and leading directly to the desired monoprotected 1,2-diol from the primary alcohol.

Combination of the three steps in a single one-pot procedure was attempted with 3-phenylpropan-1-ol **1a** as a model substrate and gave the desired product (*S*)-**4a** in good yield (49%) and enantioselectivity (91%, Table 1, entry 1).[10] The use of distilled THF as the solvent for the whole sequence allowed a slight increase of both yield and enantiomeric excess (52% and 94% respectively, entry 2). Equimolar mixture of BAIB and starting material **1a** in step one gave equivalent results (entry 3). However, loading of the alcohol was maintained to 1.1 equiv relative to $PhI(OAc)_2$ to ensure full reproducibility.[11] Lower activity was observed for catalyst (*S*)-**6** similarly to Maruoka's result[8a] (40% yield, entry 4). Decreasing the benzoylperoxide amount from 1.5 to 1.1 equiv led to the formation of (*S*)-**4a** with identical results (52% yield and 94% e.e., entry 5) compared to entry 2. The introduction of 20 mol % of catalyst (*S*)-**5** did not improve the yield and selectivity (entry 6). Finally, (±)-**4a** was secured in a 57% yield with the racemic version of Maruoka's catalyst **7**[8a] (entry 7). Due to its commercial availability in both enantiomeric forms, diphenylprolinol TMS-ether **5** was preferred for the further experiments.

Scope of this methodology was explored, first demonstrating that both enantiomers of **4a** could be produced by using (*S*)- or (*R*)-catalyst **5**, leading to (*S*)-**4a** (52% yield, 94% e.e.) and (*R*)- **4a** (49% yield, 93% e.e.) respectively (Table 2, entries 1 and 2). Then, various primary alcohols were employed as starting material. Similar results were observed with butan-1-ol **1b** (50% yield, 93% e.e., entry 3). Higher loadings of (*S*)-**5** (20 mol %) were needed to achieve the three-step sequence in correct yields when the carbon

Table 2
Scope of the oxydation/α-benzoyloxylation/reduction sequence



Entry	Alcohol	Catalyst (loading)	Product	Yield[a] (%)	e.e.[b] (%)
1	 **1a**	(*S*)-**5** (10 mol %)	 (*S*)-**4a**	52	94
2	 **1a**	(*R*)-**5** (10 mol %)	 (*R*)-**4a**	49	93
3	 **1b**	(*S*)-**5** (10 mol %)	 (*S*)-**4b**	50	93
4	 **1c**	(*S*)-**5** (20 mol %)	 (*S*)-**4c**	46	94
5	 **1d**	(*S*)-**5** (20 mol %)	 (*S*)-**4d**	39	91

(*continued on next page*)