Diastereoselective Transformations of Enol Esters Derived from Acetylenes and Chiral Carboxylic Acids

Iwona M. Kalinowska,[a] Joanna Szawkało,[a] Krzysztof K. Krawczyk,[a] Jan K. Maurin,[b,c] Zbigniew Czarnocki*[a]

[a] Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
Fax +48(22)8225996; E-mail: czarnoz@chem.uw.edu.pl

[b] National Medicines Institute, Chełmska 30/34, 00-750 Warsaw, Poland

[c] Institute of Atomic Energy, 05-400 Otwock-Świerk, Poland

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Abstract: Markovnikov-type enol esters are synthesized selectively from N-protected amino acids by ruthenium-mediated coupling with the appropriate acetylenes. Subsequent hydrogenation of the enol esters over Adams' catalyst gives the corresponding saturated products in moderate to good diastereoselectivities. The enol esters undergo reaction with *m*-chloroperoxybenzoic acid to yield α-acyloxy ketones, as the products of rearrangement, instead of the expected epoxides.

Key words: enol esters, diastereoselectivity, hydrogenation, epoxidation, ruthenium

The presence of a carbon–carbon double bond in enol esters allows their application in many different types of reactions in sustainable organic chemistry. Enol esters can be utilized effectively in [2+2], [2+4] and 1,3-dipolar cycloadditions,[1] and in cyclopropanation reactions.[2]

In 2003, Reetz and Goossen reported that complexation of a rhodium catalyst with 1,1′-bi(2-naphthol) (BINOL) derived monodentate phosphites afforded efficient catalysts for the asymmetric hydrogenation of enol esters.[3] Many other catalysts (for example, palladium, ruthenium, rhodium) and ligands have been applied in this hydrogenation giving products with high enantioselectivity (ee >90%).[4]

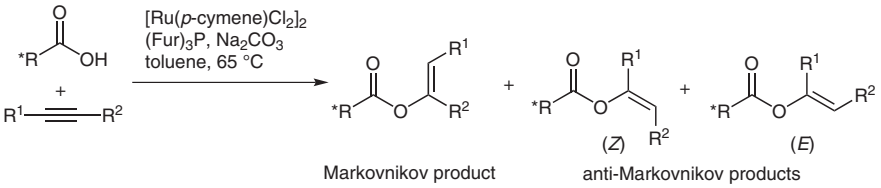
On the other hand, multicomponent reactions have become popular for the synthesis of complex structures. The Mannich-type reaction of a primary amine, an aldehyde and isopropenyl acetate under mild conditions, to yield a secondary or tertiary amine,[5] is a good example.

The bromine-catalyzed aziridination of olefins and ring-opening of aziridines has produced building blocks suitable for the synthesis of important nitrogen-containing compounds. In the case of enol esters, this reaction was examined by Sharpless who found it to be synthetically useful despite some limitations. Several electron-deficient olefins, such as α,β-unsaturated esters and amides, did not undergo this aziridination reaction.[6]

Another reaction of enol esters involves oxidation of the double bond to form epoxides. Following rearrangement promoted by Lewis acids[7] or high temperatures,[8] α-acyloxy ketones or aldehydes can be obtained.

Significant research has been devoted toward the effective and selective synthesis of enol esters. The direct functionalization of acetylenes with various carboxylic acids in the presence of a catalyst has been studied intensively for this purpose. Initial attempts employed stoichiometric amounts of mercury salts.[9] Later, the introduction of iridium[10] and rhenium[11] complexes allowed considerable reduction of the catalyst loading. However, ruthenium[12] or ruthenium–phosphine catalysts (for example, triruthenium dodecacarbonyl [$Ru_3(CO)_{12}$] and bis(cyclooctadienyl)ruthenium–tri-*n*-butylphosphine) were the most common.[13] In 2003, Moise et al. reported on the application of titanium–ruthenium heterobimetallic complexes for the synthesis of the Markovnikov enol formates.[14]

In our investigations, we synthesized the Markovnikov-type enol esters using the method reported by Goossen,[15] starting from protected amino acid derivatives and terminal or internal alkynes, with the catalyst generated in situ from dichloro(*p*-cymene)ruthenium(II) dimer [Ru(*p*-cymene)Cl_2]$_2$ as the ruthenium precursor, and tri(2-furyl)phosphine [(Fur)$_3$P] as the ligand (Scheme 1). Herein, we describe a procedure for the synthesis of chiral secondary alcohols via reduction and hydrolysis of enol esters derived from acetylenes and chiral carboxylic acids.



Scheme 1 Synthesis of enol esters

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Table 1 Synthesis of Enol Esters (Markovnikov Products) According to Scheme 1[a]

Entry	*R	R^1	R^2	Product	Time (d)	Yield (%)[b]	$[\alpha]_D^{25}$ (*c*, $CHCl_3$)
1	*N*-Cbz-L-Trp	H	C_4H_9	**1**	6	99	+11.6 (*c* 1.08)
2	*N*-Cbz-D-Trp	H	C_4H_9	**2**	5	91	–12.0 (*c* 0.88)
3	*N*-Pht-L-Ala	H	Ph	**3**	6	93	– 6.0 (*c* 1.01)
4	*N*-Pht-L-Ala	CH_2OMe	CH_2OMe	**4**	5	69	–14.0 (*c* 1.05)
5	*N*-Pht-L-Ala	Ph	Ph	**5**	10	4	– 6.6 (*c* 0.99)

[a] Reaction conditions: *RCOOH (1.6 mmol), R^1CCR^2 (2.1 mmol), Na_2CO_3 (0.04 mmol), $(Fur)_3P$ (0.02 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (0.01 mmol), toluene, 65 °C.
[b] Yield of isolated product after column chromatography.

We obtained several enol esters **1**–**5** starting from protected amino acids and the results are presented in Table 1. The selectivity in favor of the Markovnikov product was >99% in all cases. The use of L- and D-tryptophan gave, as expected, comparable results, although the increase in the yield as a result of the extended reaction time was associated with lower optical purity of the product (Table 1, entries 1 and 2).

In order to take advantage of the chiral auxiliary present in the enol ester, we next performed hydrogenation of the double bond using an achiral catalyst. Several N-protected amino acids were tested, but only with the tryptophan-containing products **1** and **2** were the diastereoselectivities of the reductions found to be promising (Scheme 2).

We established that Adams' catalyst (PtO_2) was more effective than palladium on carbon (Pd/C) or rhodium on carbon (Rh/C), however, changing the solvent or lowering the reaction temperature did not improve the diastereoselectivity. Table 2 contains selected data for the hydrogenation step.

Next, aliphatic esters **6** were hydrolyzed to yield the respective enantiomerically enriched hexan-2-ols. When the mixture of esters derived from L-tryptophan derivative **1** was hydrolyzed, (*S*)-(+)-hexan-2-ol was obtained in 69% ee, whereas D-tryptophan derivative **2** gave (*R*)-(–)-hexan-2-ol in 67% ee. These results were consistent with the HPLC analysis of the diastereomeric mixture after the hydrogenation. Isolation of ester **6a** by column chromatography and subsequent hydrolysis enabled the formation of enantiomerically pure (*S*)-(+)-hexan-2-ol. The absolute configuration of compound **6a** was confirmed unambiguously by X-ray crystal structure analysis (Figure 1).

Table 2 Hydrogenation of Compounds **1** and **2**[a]

Entry	Solvent	Substrate	Time (h)	Yield (%) of **6**[b]	**6a**/**6b**[c]	$[\alpha]_D^{25}$ (*c*, $CHCl_3$)
1	*i*-PrOH	**1**	20	84	78:22	+16.0 (*c* 0.99) (**6a**)
2	AcOH	**1**	20	80	77:23	+16.0 (*c* 0.98) (**6a**)
3	AcOH	**1**	5	80	80:20	+16.0 (*c* 1.13) (**6a**)
4	*i*-PrOH	**2**	5	78	24:76	–15.9 (*c* 0.82) (**6b**)

[a] Reaction conditions: enol ester (0.71 mmol), PtO_2 (0.071 mmol), H_2, *i*-PrOH or AcOH.
[b] Combined yield of **6a** and **6b**.
[c] Ratio determined by HPLC.

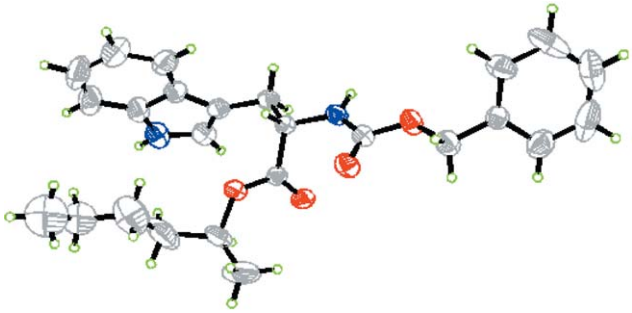
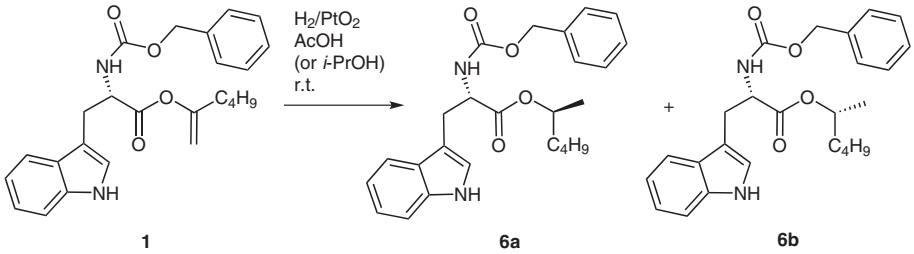
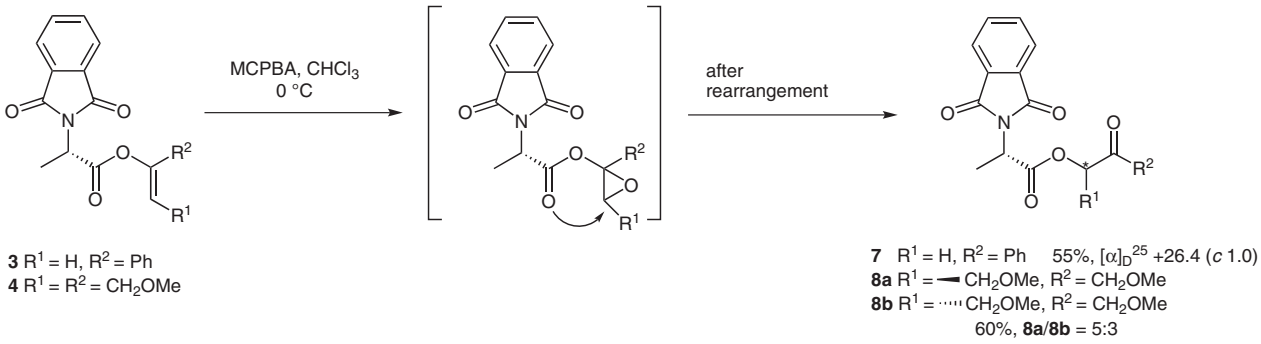


Figure 1 ORTEP diagram of **6a**[16]

In order to extend the synthetic utility of chiral enol esters to other transformations, we also studied the epoxidation of **3** and **4** with *m*-chloroperoxybenzoic acid (Scheme 3). Surprisingly, even under mild conditions (0 °C), we observed rearrangement of the initially formed epoxide into the corresponding α-acyloxy ketones **7** and **8**; generally,

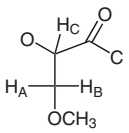


Scheme 2 Hydrogenation of compound **1**



Scheme 3 Synthesis of α-acyloxy ketones **7** and **8**

Table 3 The Observed and Simulated Chemical Shifts (δ, ppm) for Protons Near the Newly Formed Stereocenter in Diastereomers **8a** and **8b**

Compound **8**		Observed ^{1}H NMR data			Simulated ^{1}H NMR data[18] for diastereomers **8a** and **8b**		
Fragment	Proton	Major component	Minor component	Δδ	**8a** (*S*,*R*)	**8b** (*S*,*S*)	Δδ
	H_A	3.87	3.83	0.04	4.07	4.04	0.03
	H_B	3.70	3.60	0.10	3.81	3.78	0.03
	H_C	5.44	5.40	0.04	4.92	4.76	0.16

this type of rearrangement is observed at higher temperatures.[8] The structure of compound **7** was confirmed by X-ray crystal structure analysis (Figure 2). The epoxidation of enol ester **4** led to the formation of diastereomeric compounds **8a** and **8b** in the ratio 5:3 and in a combined 60% yield.

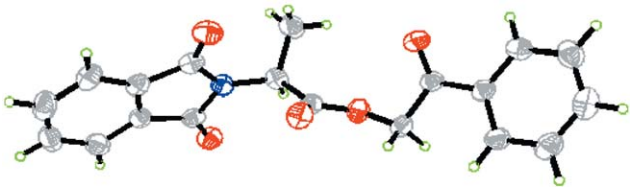


Figure 2 ORTEP diagram of **7**;[17] two independent molecules differing slightly in geometry are present in the asymmetric part of the unit cell of the crystal

Unfortunately, despite numerous attempts, we were unable to obtain a crystal suitable for X-ray analysis, and therefore the stereochemical assignments of **8a** and **8b** were based solely on analysis and simulation[18] of the ^{1}H NMR spectra. As shown in Table 3, a similar deshielding trend for protons H_A, H_B and H_C, being located in the vicinity of the newly formed stereocenter, was observed allowing tentative assignment of the stereochemistry of **8a** as *S*,*R*. This hypothesis seemed to be further supported by quantum mechanical calculations using Spartan'08 software. Initially, the four most stable conformers for both diastereomers were determined using molecular mechanics. Those conformers were then minimized using density functional theory (DFT) calculations within the 6-31G* basis set. The resulting geometries were used as an input for further density functional theory calculations, employing a more adequate cc-pVDZ basis set. The ^{1}H NMR spectra were computed within the latter. The simulated spectra for **8a** and **8b** resembled those obtained in a previous simulation approach[18] thus supporting the stereochemical assignments.

In summary, we have described new applications of enol esters in synthetic organic chemistry. The introduction of the carboxylic acid moiety allows diastereofacial functionalization of the double bond which may find applications in procedures aimed at preparing enantiomerically enriched products.

Anhydrous solvents were used for all reactions. TLC analyses were performed on silica gel plates (Merck Silica Gel 60 F_{254}) and made visual using a UV lamp and I_2 vapor. Melting points were determined on a Boetius hot-plate microscope and are uncorrected. Column chromatography was carried out at atmospheric pressure using Merck Silica Gel 60 (230–400 mesh) or Al_2O_3 using mixtures of hexane–*i*-PrOH or hexane–Et_2O as eluents. HPLC analyses were performed using Knauer (model 64) instrumentation (4 mm × 250 mm Lichrosorb Si60 column) with Eurochrom 2000 software. The NMR spectra were obtained on a Varian Unity Plus spectrometer at 200 MHz or 500 MHz for ^{1}H NMR and at 50 MHz or 125 MHz for ^{13}C NMR. The spectra were recorded in $CDCl_3$ and chemical shifts (δ) are reported in ppm relative to TMS. Mass spectra were obtained using Quattro LC Micromass and LCT Micromass TOF HiRes apparatus. Optical rotations were measured using a Perkin-Elmer 241 polarimeter. Single crystal X-ray measurements were carried out on an Oxford Diffraction Xcalibur R κ-axis diffractometer with a CCD Ruby detector. In all cases, CuKα characteristic radiation was applied. After initial corrections and data reduction, reflection intensities were used to solve and refine consecutively the structures using SHELXS97[19] and SHELXL97[20] programs. Further absorption corrections were applied in the final refinement steps.

Enol Esters 1–5; General Procedure

Protected amino acid derivative (1.6 mmol) and Na_2CO_3 (4.2 mg, 0.04 mmol) were suspended in anhyd toluene (9 mL). A soln of

(Fur)$_3$P (4.6 mg, 0.02 mmol), [Ru(*p*-cymene)Cl$_2$]$_2$ (6.1 mg, 0.01 mmol) and the acetylene (2.1 mmol) in anhyd toluene (2 mL) was added. The mixture was heated at 65 °C until TLC indicated complete conversion of the amino acid derivative. The solvent was evaporated and the residue dissolved in $CHCl_3$ (10 mL). The organic layer was washed with sat. aq $NaHCO_3$ soln (3 × 4 mL) and dried over anhyd $MgSO_4$. The solvent was removed and the product purified by column chromatography over silica gel (eluent: hexane–*i*-PrOH).

Hex-1-en-2-yl *N*-Carbobenzyloxytryptophanate (1)

Yellow solid; yield: 1.33 g (99%); mp 58–61 °C; $[\alpha]_D^{25}$ +11.6 (*c* 1.08, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (br s, 1 H), 7.58 (d, *J* = 7.8 Hz, 1 H), 7.37–7.28 (m, 5 H), 7.19 (t, *J* = 7.1 Hz, 1 H), 7.10 (t, *J* = 7.5 Hz, 1 H), 7.00–6.99 (m, 1 H), 5.33 (d, *J* = 8.3 Hz, 1 H), 5.12 (d, *J* = 12.5 Hz, 1 H), 5.08 (d, *J* = 12.5 Hz, 1 H), 4.80–4.77 (m, 1 H), 4.68 (br s, 1 H), 4.60 (br s, 1 H), 3.39–3.31 (m, 2 H), 2.09–2.04 (m, 2 H), 1.62 (s, 1 H), 1.37–1.25 (m, 4 H), 0.86 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.3, 156.4, 155.7, 136.3, 136.1, 128.5, 128.2, 128.1, 127.6, 122.8, 122.3, 119.8, 118.8, 111.2, 109.8, 101.3, 66.9, 54.7, 32.8, 28.4, 27.9, 22.0, 13.8.

MS (ESI+): *m*/*z* (%) = 443.2 (100) [M + Na]$^+$, 863.4 (15) [2M + Na]$^+$.

1,4-Dimethoxybut-2-en-2-yl (2*S*)-2-(1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl)propanoate (4)

Yellow oil; yield: 1.15 g (69%); $[\alpha]_D^{25}$ –14.0 (*c* 1.05, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.91–7.83 (m, 2 H), 7.79–7.72 (m, 2 H), 5.59 (t, *J* = 7.3 Hz, 1 H), 5.09 (q, *J* = 7.1 Hz, 1 H), 4.14–3.92 (m, 4 H), 3.33 (s, 3 H), 3.29 (s, 3 H), 1.72 (d, *J* = 7.1 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.5, 167.4, 148.0, 134.4, 132.1, 123.2, 119.6, 67.7, 66.7, 58.4, 58.1, 47.5, 15.5.

MS (ESI+): *m*/*z* (%) = 356.1 (100) [M + Na]$^+$, 372.1 (10) [M + K]$^+$, 689.2 (27) [2M + Na]$^+$.

Hydrogenation of Enol Esters 1–5; General Procedure

The enol ester (0.71 mmol) was dissolved in *i*-PrOH (or AcOH) (6 mL) and PtO_2 (16.2 mg, 0.071 mmol) was suspended in the mixture. The suspension was stirred under H_2 for 20 h (or 5 h) at r.t. The catalyst was removed by filtration and the solvent evaporated. The residue was dissolved in $CHCl_3$ (6 mL), washed with a small amount of sat. aq $NaHCO_3$ soln (2 mL) and dried over anhyd $MgSO_4$. The solvent was evaporated and the residue purified by silica gel column chromatography (eluent: hexane–*i*-PrOH).

(1*S*)-1-Methylpentyl *N*-Carbobenzyloxy-l-tryptophanate (6a); Table 2, Entry 3

Compound **1** (0.4 g, 0.95 mmol) was dissolved in AcOH (6 mL) and PtO_2 (21.6 mg, 0.095 mmol) was suspended in the mixture. The mixture was stirred under H_2 for 5 h at r.t. Product **6a** was purified by silica gel column chromatography (eluent: hexane–*i*-PrOH, 9:1) and subsequently recrystallized from Et_2O–hexane.

White solid; yield: 0.257 g (64%); mp 104–106 °C; $[\alpha]_D^{25}$ +16.0 (*c* 1.13, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.04 (br s, 1 H), 7.56 (d, *J* = 8.3 Hz, 1 H), 7.37–7.27 (m, 6 H), 7.19–7.16 (m, 1 H), 7.10–7.06 (m, 1 H), 5.32–5.28 (m, 1 H), 5.13–5.05 (m, 2 H), 4.89–4.83 (m, 1 H), 4.70–4.67 (m, 1 H), 3.34–3.23 (m, 2 H), 1.60–1.58 (m, 1 H), 1.54–1.46 (m, 2 H), 1.43–1.36 (m, 1 H), 1.24–1.23 (m, 3 H), 1.14–1.10 (m, 3 H), 0.89–0.83 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.7, 155.8, 136.4, 136.1, 128.5, 128.2, 122.7, 122.3, 119.7, 118.9, 111.1, 110.2, 72.7, 66.9, 65.7, 54.7, 35.4, 31.7, 27.3, 22.4, 19.7, 13.9.

MS (ESI+): *m*/*z* (%) = 445.2 (100) [M + Na]$^+$, 867.4 (20) [2M + Na]$^+$.

(*S*)-(+)-Hexan-2-ol

Compound **6a** (0.046 g, 0.11 mmol) was added to a mixture of H_2O (2 mL), EtOH (2 mL) and KOH (0.4 g). The resulting mixture was heated at reflux temperature until ester **6a** had been consumed (TLC) and was then extracted with $CHCl_3$ (2 × 1 mL). The combined organic phase was dried over anhyd $MgSO_4$ and evaporated to afford (*S*)-(+)-hexan-2-ol.

Colorless liquid; yield: 6 mg (54%); ee >98%; $[\alpha]_D^{25}$ +11.8 (*c* 0.56, $CHCl_3$) {Lit.[21] $[\alpha]_D^{25}$ +12.0 (*c* 0.2, $CHCl_3$)}. All other analytical data were consistent with those reported in the literature.[21]

2-Oxo-2-phenylethyl (2*S*)-2-(1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl)propanoate (7)

Enol ester **3** (0.4 g, 1.3 mmol) was dissolved in $CHCl_3$ (2 mL) and added dropwise to a soln of MCPBA (0.210 g, 2.6 mmol) in $CHCl_3$ (8 mL) at 0 °C. The mixture was stirred at r.t. for 3 d. The organic layer was washed with 10% aq $NaHCO_3$ soln (3 × 4 mL), dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography on silica gel (hexane–*i*-PrOH, 20:1).

White solid; yield: 0.24 g (55%); mp 133–135 °C; $[\alpha]_D^{25}$ +26.4 (*c* 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89–7.85 (m, 4 H), 7.76–7.72 (m, 2 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.8 Hz, 2 H), 5.44 (d, *J* = 16.5 Hz, 1 H), 5.33 (d, *J* = 16.5 Hz, 1 H), 5.21 (q, *J* = 7.3 Hz, 1 H), 1.79 (d, *J* = 7.3 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.3, 169.3, 167.3, 134.2, 134.1, 133.9, 132.0, 128.9, 127.8, 123.6, 66.9, 47.5, 15.3.

MS (ESI+): *m*/*z* (%) = 360.1 (100) [M + Na]$^+$.

(2*R*)-1,4-Dimethoxy-3-oxobutan-2-yl (2*S*)-2-(1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl)propanoate (8a) and (2*S*)-1,4-Dimethoxy-3-oxobutan-2-yl (2*S*)-2-(1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl)propanoate (8b)

Enol ester **4** (0.3 g, 0.92 mmol) was dissolved in $CHCl_3$ (8 mL) and added dropwise to a soln of MCPBA (0.32 g, 1.9 mmol) in $CHCl_3$ (2 mL) at 0 °C. The mixture was stirred at r.t. for 5 d. The organic layer was washed with 10% aq $NaHCO_3$ soln (3 × 4 mL) and dried over $MgSO_4$. Residual MCPBA was removed by column chromatography over basic Al_2O_3 (eluent: $CHCl_3$). The solvent was evaporated and the residue subjected to column chromatography over silica gel (eluent: hexane–Et_2O, 1:1) to afford α-acyloxy ketones **8a** and **8b** as a 5:3 mixture of diastereomers in 60% combined yield.

White solid; yield: 0.19 g (60%); mp 121–129 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ (major component, **8a**) = 7.89–7.87 (m, 2 H), 7.76–7.75 (m, 2 H), 5.44 (dd, J_1 = 4.9, J_2 = 3.4 Hz, 1 H), 5.13 (q, *J* = 7.3 Hz, 1 H), 4.15 (d, *J* = 18.0 Hz, 1 H), 4.09 (d, *J* = 18.0 Hz, 1 H), 3.87 (dd, J_1 = 10.8, J_2 = 4.9 Hz, 1 H), 3.70 (dd, J_1 = 10.8, J_2 = 3.4 Hz, 1 H), 3.35 (s, 3 H), 3.32 (s, 3 H), 1.77 (d, *J* = 7.3 Hz, 3 H).

^{1}H NMR (500 MHz, $CDCl_3$): δ (minor component, **8b**) = 7.87–7.86 (m, 2 H), 7.75–7.73 (m, 2 H), 5.40 (dd, J_1 = 4.9, J_2 = 2.8 Hz, 1 H), 5.11 (q, *J* = 7.3 Hz, 1 H), 4.22 (d, *J* = 17.5 Hz, 1 H), 4.19 (d, *J* = 17.5 Hz, 1 H), 3.83 (dd, J_1 = 11.3, J_2 = 4.3 Hz, 1 H), 3.60 (dd, J_1 = 10.7, J_2 = 3.5 Hz, 1 H), 3.42 (s, 3 H), 3.22 (s, 3 H), 1.76 (d, *J* = 7.3 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ (diastereomeric mixture) = 202.4, 202.2, 169.1, 167.3, 167.2, 134.3, 134.2, 131.8, 123.6, 123.5, 77.6, 76.3, 76.2, 77.1, 71.0, 59.5, 59.4, 59.2, 47.5, 47.4, 15.2.

MS (ESI+): *m*/*z* (%) = 372.0 (100) [M + Na]$^+$, 388.0 (3) [M + K]$^+$, 721.1 (6) [2M + Na]$^+$.

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References

(1) (a) Wexler, A.; Balchunis, R. J.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1975**, 601. (b) Jung, M. E.; Hudspeth, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4309. (c) Pirrung, M. C.; Lee, Y. R. *Tetrahedron Lett.* **1994**, *35*, 6231.
(2) Motherwell, W. B.; Roberts, L. R. *J. Chem. Soc., Chem. Commun.* **1992**, 1582.
(3) Reetz, M. T.; Goossen, L. J.; Meiswinkel, A.; Paetzold, J.; Jensen, J. F. *Org. Lett.* **2003**, *5*, 3099.
(4) For example, see: (a) Boaz, N. W. *Tetrahedron Lett.* **1998**, *39*, 5505. (b) Tang, W.; Liu, D.; Zhang, X. *Org. Lett.* **2003**, *5*, 205. (c) Wu, S.; Wang, W.; Tang, W.; Lin, M.; Zhang, X. *Org. Lett.* **2002**, *4*, 4495. (d) Szőri, K.; Szöllősi, G.; Felföldi, K.; Bartók, M. *React. Kinet. Catal. Lett.* **2005**, *84*, 151.
(5) Isambert, N.; Cruz, M.; Arévalo, J.; Gómez, E.; Lavilla, R. *Org. Lett.* **2007**, *9*, 4199.
(6) Jeong, J. U.; Tao, B.; Sagasser, I.; Henniges, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1998**, *120*, 6844.
(7) Feng, X.; Shi, Y. *J. Org. Chem.* **2002**, *67*, 2831.
(8) Draper, A. L.; Heilman, W. J.; Schaepfer, W. E.; Shine, H. J.; Shoolery, J. N. *J. Org. Chem.* **1962**, *27*, 2727.
(9) (a) Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966. (b) Bach, R. D.; Woodard, R. A.; Anderson, T. J.; Glick, M. D. *J. Org. Chem.* **1982**, *47*, 3707.
(10) Nakagawa, H.; Okimoto, Y.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **2003**, *44*, 103.
(11) Hua, R.; Tian, X. *J. Org. Chem.* **2004**, *69*, 5782.
(12) Rotem, M.; Shvo, Y. *Organometallics* **1983**, *2*, 1689.
(13) (a) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1566. (b) Ruppin, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1988**, *29*, 5365.
(14) Le Gendre, P.; Comte, V.; Michelot, A.; Moise, C. *Inorg. Chim. Acta* **2003**, *350*, 289.
(15) Goossen, L. J.; Paetzold, J.; Koley, D. *Chem. Commun.* **2003**, 706.
(16) The detailed structural parameters have been deposited with the Cambridge Crystallographic Data Centre (CCDC 805409).
(17) The detailed structural parameters have been deposited with the Cambridge Crystallographic Data Centre (CCDC 805410).
(18) MestReNova software, v. 6.2.1–7569, 2010, Mestrelab Research SL, Santiago de Compostela, Spain.
(19) Sheldrick, G. M. *SHELXS97. Program for solving crystal structures*; University of Gottingen: Germany, **1997**.
(20) Sheldrick, G. M. *SHELXL97. Program for crystal structure refinement*; University of Gottingen: Germany, **1997**.
(21) Tanaka, K.; Honke, S.; Urbańczyk-Lipkowska, Z.; Toda, F. *Eur. J. Org. Chem.* **2000**, 3171.