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Hydration of Acetylenic Esters: Synthesis of β-Keto-Esters

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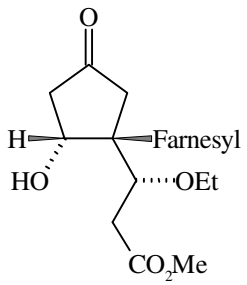
Abstract

Acetylenic esters, which are easily prepared by carbethoxylation of terminal acetylenes, can be hydrated regioselectively to β-keto-esters. In this paper, the terminal acetylenes were prepared by addition of lithium acetylide (complexed with ethylenediamine) to epoxides of cyclopentane derivatives to produce compounds oxygenated at the same position as certain natural products from *Otoba parvifolia*. The hydration was carried out by two different processes, producing either δ-oxygenated or γ,δ-unsaturated β-keto-esters.

Keywords: Acetylenic esters, hydration, β-keto-esters, cyclopentane derivatives, lithium acetylide

Introduction

The Brazilian plant *Otoba parvifolia* from the Amazon valley has proved to be a rich source of cyclopentane-based natural products with novel and unusual structures, such as **1**, which shows the typical oxygenation pattern.[1] We have been interested for some time in the synthesis of these natural products, and one route we have been exploring to **1** is *via* the corresponding β-keto-esters. We describe here our results on the synthesis of cyclopentyl and cyclopentenyl substituted β-keto esters related to **1**.



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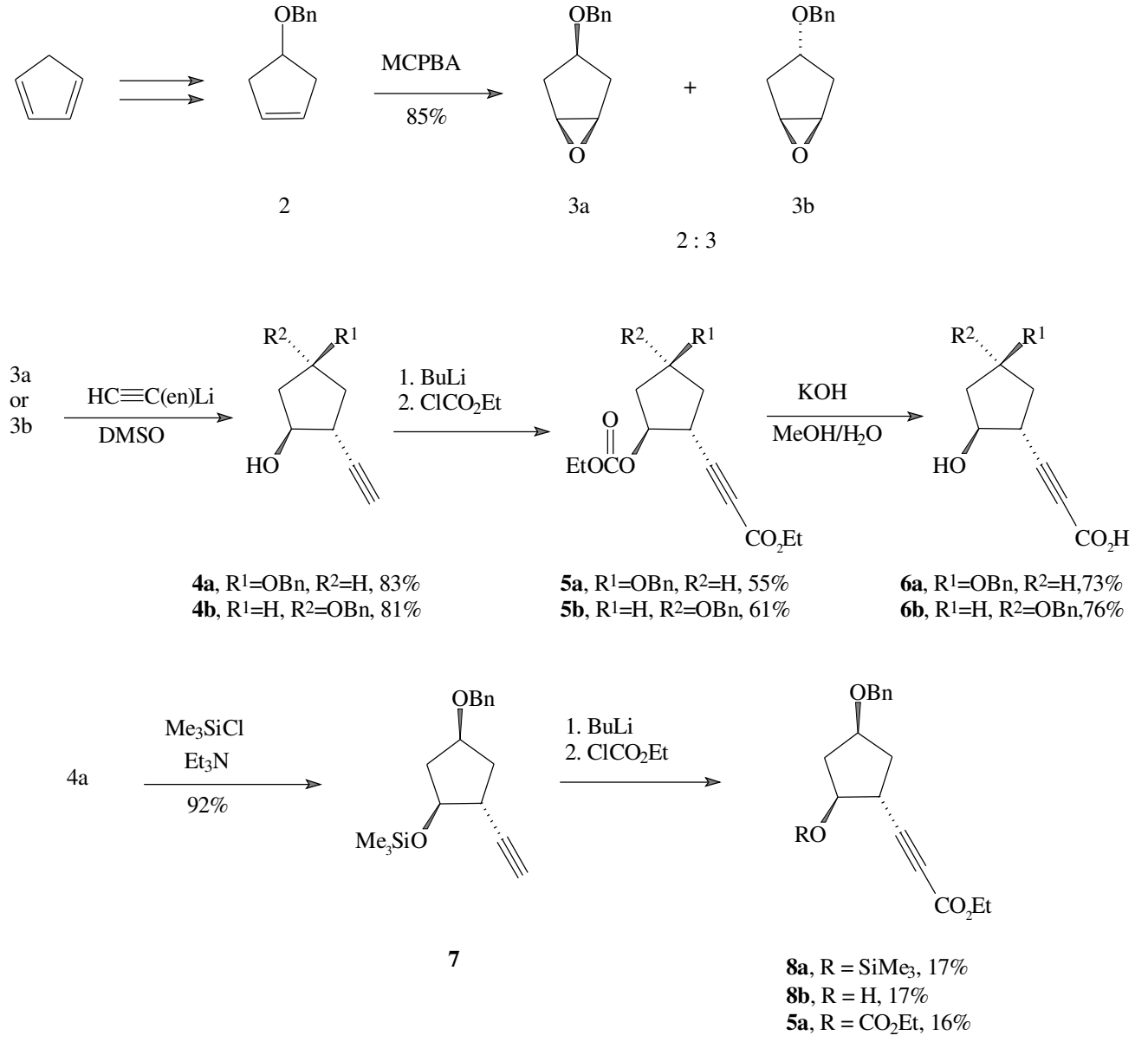
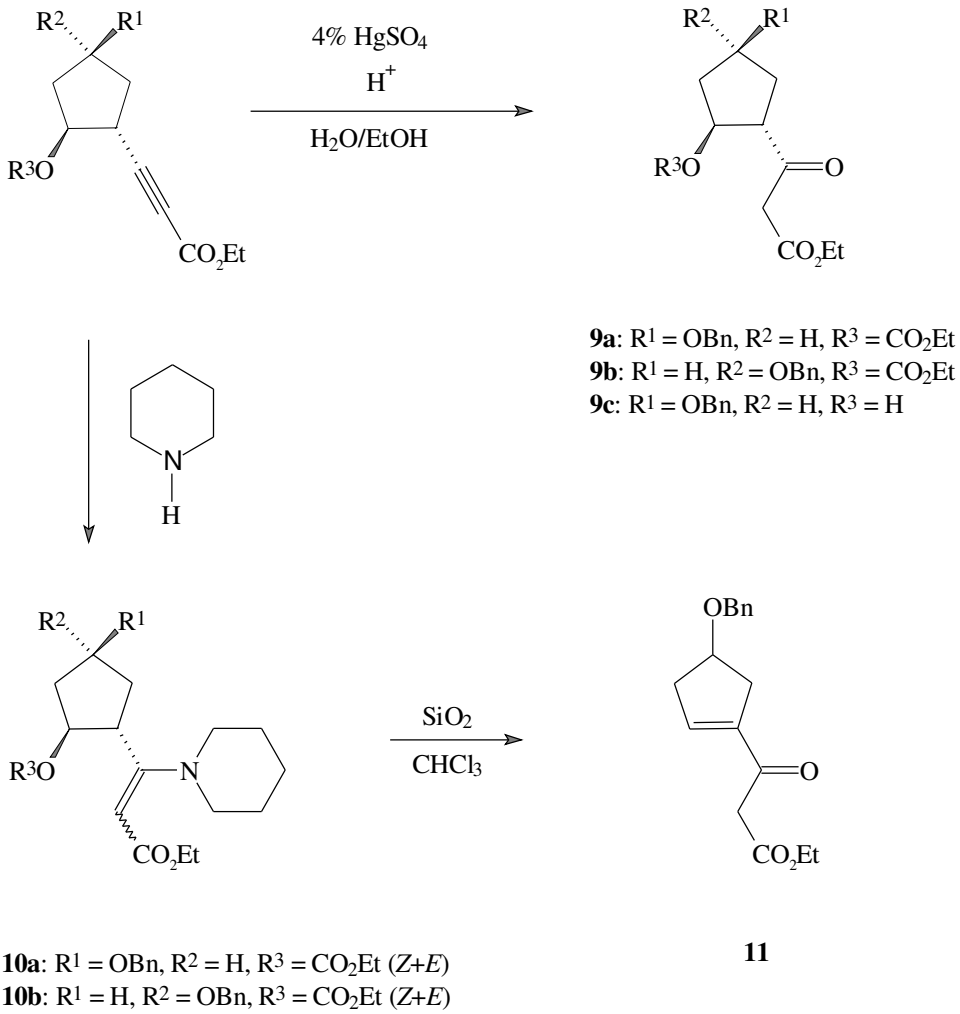


Scheme 1. *Preparation of acetylenic esters*

Our general approach is outlined in Scheme 1. Hydroboration-oxidation of cyclopentadiene was performed by the procedure described by Allred,[2] with minor modifications, and treatment of the resulting cyclopentenol with sodium hydride in dioxane, followed by benzyl chloride, [3] produced the ether **2.** Oxidation of **2** with *m*-chloroperbenzoic acid [4] furnished, as expected, a mixture of two stereoisomers **3a** and **3b** in a ratio of 2:3. The isomers were separated by column chromatography and the subsequent reactions were performed exclusively with pure isomers.

Treatment of the epoxides **3a** or **3b** either with sodium acetylide or with the anions from methyl propiolate or from propiolic acid resulted only in the recovery of starting material, thus confirming the conclusion by Murray [5] that simple acetylide anions are not suitable for the nucleophilic opening of epoxides of cyclic olefins. By contrast, use of lithium acetylide complexed with ethylenediamine in DMSO resulted in a clean and smooth reaction with the epoxides **3a** or **3b** to give compounds **4a** and **4b** in yields of 83 and 81%, respectively.[6]

Although direct carboxylation of the dianion from either **4a** or **4b** could not be effected, carbethoxylation of the same dianions with ethyl chloroformate [7] proved easy. Compounds **5a** and **5b,** the desired acetylenic esters, were obtained after the original cyclopentanol hydroxyl group was converted to a carbonate ester. We have also demonstrated that compounds **6a** and **6b,** the expected products



9a: R^1 = OBn, R^2 = H, R^3 = CO_2Et
9b: R^1 = H, R^2 = OBn, R^3 = CO_2Et
9c: R^1 = OBn, R^2 = H, R^3 = H

10a: R^1 = OBn, R^2 = H, R^3 = CO_2Et (*Z*+*E*)
10b: R^1 = H, R^2 = OBn, R^3 = CO_2Et (*Z*+*E*)

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Scheme 2. *Hydration of acetylenic esters*

of direct carboxylation of **4a** and **4b,** can be prepared in good yield by saponification of **5a** and **5b**.

The acetylenic ester **8a,** which contains the trimethylsilyloxy group at the δ-position, was prepared in a similar way by carbethoxylation of the silyl ether **7**, itself easily obtained from **4a**. A small amount (16%) of the carbonate ester **5a** was also formed during the reaction, but formation of the alcohol **8b** probably occurred during purification by column chromatography.

Hydration of the acetylenic esters was performed as summarized in Scheme 2 and Table 1, either by treatment with mercuric sulfate and acid [8], or by conjugate addition of piperidine followed by acid hydrolysis of the resulting enamine.[9]

It is worth noting that, in preliminary experiments using a slightly different starting material (containing -OTHP instead of -OBn), we found that formic acid is a poor hydrating agent for these acetylenic esters, in contrast to the good results we had previously obtained with formic acid in the hydration of diacetylenic compounds.[10,11]

The hydration with acidic aqueous/ethanolic mercuric sulfate proved to be an efficient reaction for each of the acetylenic esters we used. When methanol was used as solvent, some ester exchange was observed. The carbonate group (R_3) is stable under these hydration conditions, as is the benzyloxy group, but the trimethylsilyl group is, as expected, hydrolysed during the reaction.

The two-step hydration protocol, which consists of conjugate addition of piperidine to produce a diastereo-isomeric (*Z* + *E*) mixture of enamines followed by acidic hydrolysis, while using very mild conditions in the first step, invariably proceeded with elimination of the carbonate group during the hydrolysis of the enamine. Even with the very gentle conditions of silica gel and chloroform, **11** was still the only product that could be isolated. γ,δ-unsaturated compounds, such as **11**, should prove to be useful intermediates in the synthesis of many natural products. However, if δ-oxygenated β-ketoesters of the type **1** are desired, then clearly hydration of the corresponding

Table 1. *Hydration of Acetylenic Esters (see Scheme 2)*

Reagent	Starting Material **A**	R_1	R_2	R_3	Product	Yield, %	Yield of **11**, %
$HgSO_4$	**5a**	OBn	H	CO_2Me	**9a**	71	-
	5b	H	OBn	CO_2Me	**9b**	74	-
	8a	OBn	H	$SiMe_3$	**9c**	96	-
	8b	OBn	H	H	**9c**	90	-
piperidine	**5a**	OBn	H	CO_2Me	**10a**	100	77
					(*Z*+*E*)	(crude)	77
	5b	H	OBn	CO_2Me	**10b**	100	75
					(*Z*+*E*)	(crude)	

acetylenic esters should be by treatment with mercuric sulfate.

The high regioselectivity of the hydration reaction is remarkable, and is determined by the ester group.[11] No α-keto esters were observed in any of our hydration reactions.

Experimental section

NMR spectra were measured using a Bruker AC-80 (80 MHz ^{1}H-NMR, and 20 MHz ^{13}C-NMR) or a Varian EM360L (60 MHz; ^{1}H-NMR) instrument; deuterochloroform and carbon tetrachloride were used as solvents, and tetramethylsilane as the internal standard. IR spectra were measured with a Perkin-Elmer 1430 or a Perkin-Elmer 1600 FT spectrometers. TLC was performed on precoated silica gel 60 F_{254} plates (0.25 mm thick, Merck), and for column chromatography silica gel 60 70-230 mesh (Merck) was used.

3-Cyclopentenol [2]

Diborane, produced as described by Zweifel and Brown [13] from $NaBH_4$ (13.6 g, 0.358 mol) and $BF_3.Et_2O$ (104 g, 0.732 mol) in diglyme, was passed through a solution of freshly distilled cyclopentadiene (159 g, 2.41 mol) in THF (400 mL) maintained at 0°C with mechanical stirring. After the addition of diborane was completed, the reaction mixture was stirred at room temperature for 1 h. The solvent and excess cyclopentadiene were removed under vacuum and the viscous residue was cooled with an ice bath and treated with a 3 N aqueous solution of NaOH (200 mL) followed by a 30% solution of H_2O_2 (220 mL). The product was extracted with ether and the organic phase was dried with $MgSO_4$. After removing the solvent under vacuum, the residue was distilled at 71-73°C (30 mm Hg). Yield 24.6 g (0.293 mol, 21 % based on the amount of diborane). IR (neat film) 3375, 1610, 1107 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 2.05-2.80 (4H, dd), 3.95 (1H, br.s), 4.25-4.55 (1H, m), 5.60 (2H, s); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 42.0 (CH_2), 70.9 (CH), 127.9 (CH).

*3-Benzyloxy-l-cyclopentene (**2**) [3]*

To sodium hydride (3.15 g of a 60 % dispersion in mineral oil, previously washed with hexane, 78.7 mmol), maintained under nitrogen atmosphere, was added a solution of 3-cyclopentenol (3.0 g, 35.7 mmol) in dry dioxane (320 mL). The reaction mixture was heated to reflux for 2 h and then cooled with an ice bath, benzyl chloride (5.7 g, 45.0 mmol) was added dropwise and the mixture was heated again to reflux for 21 h. After cooling to room temperature, the reaction mixture was poured onto ice, and the product was extracted with ether. The organic layer was separated and dried with $MgSO_4$. The solvent was removed under vacuum and the residue was distilled at 100°C (5 mmHg). Yield 4.6 g (26.7 mmol, 75 %). IR (neat film) 1610, 1095, 1072, 735, 696 cm^{-1}; ^{1}H-NMR (CCl_4, 80 MHz) δ 2.35-2.60 (4H, m), 4.05-4.40 (1H, m), 4.45 (2H, s), 5.60 (2H, s), 7.25 (5H, s); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 39.3 (CH_2), 70.8 (CH_2), 78.8 (CH), 127.4 (CH), 127.7 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 138.8 (C).

*cis-3-(Benzyloxy)-6-oxabicyclo[3.1.0]hexane (**3a**) and trans-3-(Benzyloxy)-6-oxabicyclo[3.1.0]hexane (**3b**) [4, 14]*

To an ice-cooled solution of compound **2** (874 mg, 5.02 mmol) in methylene chloride (3.7 mL) was added a solution of *m*-chloroperbenzoic acid (1.14 g of 80% MCPBA, 6.60 mmol) in methylene chloride (11.3 mL) from a dropping funnel. The ice bath was removed and the stirring

was continued for 2 h at room temperature. The resulting mixture was treated with 10% sodium sulfite (40 mL) and stirred for 30 min. The organic phase was separated and washed with 5% $NaHCO_3$, water and saturated aqueous NaCl. The mixture was dried ($MgSO_4$) and concentrated to dryness under reduced pressure. The residue was applied to a silica gel column and eluted with (7:3) hexane-ethyl acetate. The *trans* and *cis* isomers were isolated in 472 mg (2.48 mmol, 49 %) and 340 mg (1.79 mmol, 36 %) yield, respectively. *cis*-Isomer **3a:** IR (neat film) 1095, 790, 738, 698 cm^{-1}; ^{1}H-NMR (CCl_4, 80 MHz) δ 1.6-2.25 (4H, m), 3.30 (2H, s), 3.85-4.15 (1H, m), 4.30 (2H, s), 7.15 (5H, s); ^{13}C-NMR (CCl_4, 20 MHz) δ 34.9 (CH_2), 56.7 (CH), 70.3 (CH_2), 78,5 (CH), 126.9 (CH), 127.2 (CH), 127.9 (CH), 138.6 (C). *trans*-Isomer **3b:** IR (neat film) 1111, 791, 738, 699 cm^{-1}; ^{1}H-NMR (CCl_4, 80 MHz) δ 1.40-1.75 (2H, dd), 2.20-2.60 (2H, dd), 3.30 (2H, s), 3.55-3.95 (1H, m), 4.35 (2H, s), 7.20 (5H, s), ^{13}C-NMR (CCl_4, 20 MHz) δ 34.3 (CH_2), 54.6 (CH), 71.5 (CH_2), 75.8 (CH), 127.2 (CH), 127.2 (CH), 128.0 (CH), 138.5 (C).

*(1S, 2R, 4S)-2-Ethynyl-4-benzyloxy-cyclopentanol (**4a**) and its enantiomer (racemic mixture) [5]*

To a solution of compound **3a** (265 mg, 1.39 mmol) in dry DMSO (0.9 mL) under nitrogen was added lithium ethylenediamine (400 mg, 4.4 mmol) all at once. The mixture was stirred at room temperature for 20 h and then was hydrolysed with a saturated aqueous NH_4Cl and extracted with ether. The ether fractions were washed with saturated aqueous NH_4Cl, dried over $MgSO_4$ and evaporated under reduced pressure. The product was purified by column chromatography (silica gel), eluting with (7:3) chloroform-diisopropyl ether. Yield 249 mg (1.15 mmol, 83 %). IR (neat film) 3400, 3300, 2114, 1096, 738, 698 cm^{-1}; ^{1}H-NMR (CCl_4, 80 MHz) δ 1.60-2.45 (5H, m), 2.65-3.10 (2H, m), 3.85-4.20 (2H, m), 4.40 (2H, s), 7.20 (5H, s); ^{13}C-NMR (CCl_4, 20 MHz) δ 37.6 (CH), 40.0 (CH_2), 69.9 (CH), 70.6 (CH_2), 77.7 (CH), 78.4 (CH), 86.2 (C), 126.7 (CH), 127.4 (CH), 128.0 (CH), 138.1 (C).

*(1S, 2R, 4R)-2-Ethynyl-4-benzyloxy-cyclopentanol (**4b**) and its enantiomer (racemic mixture)*

This compound was prepared as described for **4a,** starting with oxirane **3b** but stirring at room temperature for a longer time (40 h). Yield 244 mg (1.13 mmol, 81%). IR (neat film) 3400, 3300, 2115, 1100, 738, 698 cm^{-1}; ^{1}H-NMR (CCl_4, 80 MHZ) δ 1.50-2.60 (6H, m), 3.40 (1H, br.s), 3.80-4.40 (2H, m), 4.45 (2H, s), 7.20 (5H, s), ^{13}C-NMR ($CC1_4$, 20 MHz) δ 37.5 (CH), 40.3 (CH_2), 70.0 (CH), 70.7 (CH_2), 76.9 (CH), 86.0 (C), 127.3 (CH), 127.4 (CH), 128.1 (CH), 138.4 (C).

*(1S, 2R, 4S)-2-Carbethoxyethynyl-4-benzyloxy-cyclopentyl carbonate (**5a**) and its enantiomer (racemic mixture [7])*

To a stirred solution of compound **4a** (796 mg, 3.68 mmol) in THF (6.0 mL) and HMPA (2.25 mL) cooled to -78°C was added n-butyllithium in hexane (9.22 mL, 10.6 mmol, 1.15 M). Stirring was then continued for 1 h, after which was added a solution of ethyl chloroformate (1610 mg, 14.9 mmol) in anhydrous THF (4 mL), previously cooled to -78°C. The mixture was stirred for 2 h and then the temperature was allowed to rise gradually to room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl and then extracted with ether. The ether extract was washed with saturated NH_4Cl solution and water, dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a silica gel column eluting with (7:3) hexane-ethyl acetate. Yield 723 mg (2.00 mmol, 55 %). IR (neat film) 2237, 1745, 1711, 1261, 751, 698 cm^{-1}; ^{1}H-NMR (CCl_4, 80 MHz) δ 1.10-1.40 (6H, dt), 1.70-2.65 (4H, m), 3.00-3.50 (1 H, m), 3.90-4.30 (5H, m), 4.45 (2H, s), 4.75-5.10 (1H, m), 7.20 (5H, s); ^{13}C-NMR (CCl_4, 20 MHz) δ 14.0 (CH_3), 14.1 (CH_3), 34.4 (CH), 37.1 (CH_2), 38.0 (CH_2), 60.8 (CH_2), 63.2 (C), 70.5 (CH_2), 77.0 (CH), 80.8 (CH), 86.6 (C), 127.1 (CH), 128.0 (CH), 138.0 (C), 152.1 (CO), 153.9 (CO).

*(1S, 2R, 4R)-2-Carbethoxyethynyl-4-benzyloxy-cyclopentyl carbonate (**5b**) and its enantiomer (racemic mixture)*

This compound was prepared in a manner identical with that of **5a,** starting with compound **4b.** Yield 814 mg (2.25 mmol, 61 %). IR (neat film) 2236, 1747, 1711, 1256, 751, 698 cm^{-1}, ^{1}H-NMR (CCl_4, 80 MHz) δ 1.10-1.40 (6H, t), 1.75-2.60 (4H, m), 2.75-3.05 (1H, m), 3.90 - 4.30 (5H, m), 4.40 (2H, s), 4.95-5.20 (1H, m), 7.20 (5H, s); ^{13}C-NMR (CCl_4, 20 MHz) δ 14.0 (CH_3), 14.2 (CH_3), 34.6 (CH), 36.7 (CH_2), 38.5 (CH_2), 60.8 (CH_2), 63.3 (C), 70.7 (CH_2), 77.3 (CH), 81.2 (CH), 87.0 (C), 127.0 (CH), 127.3 (CH), 128.1 (CH), 138.1 (C), 153.5 (CO), 154.2 (CO).

*(1S,2R,4S)-2-Carboxyethynyl-4-benzyloxy-cyclopentanol (**6a**) and its enantiomer (racemic mixture)*

A mixture of compound **5a** (94 mg, 0.261 mmol), 3.9% aqueous solution of KOH (0.47 mL) and MeOH (0. 12 mL) was refluxed for 75 min, after which the MeOH was removed under reduced pressure from the mixture. Water was added to the residue and the aqueous layer was washed three times with ether and then acidified with conc. HCl. The product was extracted with ether, the ether fraction was dried with $MgSO_4$ and the solvent was evaporated. Yield 49 mg (0.187 mmol, 73 %). IR (neat film) 3380, 2236, 1710, 738, 698 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 1.70-2.50 (4H, m), 2.90-3.20 (1H, m), 3.95-4.40 (2H, m), 4.50 (2H, s), 6.60 (1H, br.s), 7.30 (5H, s).

*(1S, 2R, 4R)-2-Carboxyethynyl-4-benzyloxy-cyclopentanol (**6b**) and its enantiomer (racemic mixture)*

This compound was prepared as described for **6a,** starting with compound **5b** but stirring at reflux temperature for a longer time (4 h). Yield 52 mg (0.198 mmol, 76 %). IR (neat film) 3400, 2230, 1705, 745, 698 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 1.60-2.85 (5H, m), 3.90-4.25 (2H, m), 4.45 (2H, s), 6.65 (1H, br.s), 7.30 (5H, s); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 36.7 (CH), 37.4 (CH_2), 40.1 (CH_2), 71.2 (CH_2), 76.8 (CH), 91.7 (CH), 127.9 (CH), 128.5 (CH), 137.7 (C), 156.1 (CO).

*(1S, 2R, 4S)-1-Trimethylsilyloxy-2-ethynyl-4-benzyloxy-cyclopentane (**7**) and its enantiomer (racemic mixture)[15]*

To a solution of compound **4a** (216 mg, 1.0 mmol) in dry THF (2.2 mL) was added Et_3N (121 mg, 1.20 mmol) and Me_3SiCl (109 mg, 0.13 mL, 1.0 mmol). The reaction mixture was stirred for 7 h at room temperature, after which it was concentrated under reduced pressure. The crude product was diluted with ether, filtered to remove $Et_3NH^+Cl^-$, and concentrated under reduced pressure. Yield 266 mg (0.923 mmol, 92%). ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 0.15 (9H, s), 1.50-3.00 (6H, m), 3.80-4.20 (2H, m), 4.45 (2H, s), 7.30 (5H, s).

*(1S, 2R, 4S)-1-Trimethylsilyloxy-2-carbethoxyethynyl-4-benzyloxy-cyclopentane (**8a**) and its enantiomer (racemic mixture) [8]*

The reaction was performed as previously described for the compound **5a,** using compound **7** (266 mg, 0.922 mmol) in THF (0.8 mL), HMPA (0.55 mL), n-butyllithium in hexane (0.59 mL, 1.31 mmol, 2.25 M) and a solution of ethyl chloroformate (200 mg, 1.84 mmol) in THF (0.8 mL). The crude product (266 mg, 0.737 mmol, 80 %) was purified by column chromatography on silica gel with (7:3) hexane-ethyl acetate. Yield 57 mg (0.157 mmol, 17 %). ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 0.15 (9H, s), 1.15-1.40 (3H, t), 1.50-2.55 (4H, m), 2.75-3.00 (1 H, m), 3.80-4.35(4H, m), 4.40 (2H, s), 7.30 (5H, s).

*(1S, 2S, 4S)-2-Carbethoxyacetyl-4-benzyloxy-cyclopentyl carbonate (**9a**) and its enantiomer (racemic mixture) [7]*

To a solution of **5a** (300 mg, 0.83 mmol) in ethanol (4.3 mL) was added an aqueous solution of 4% $HgSO_4$ (1.3 mL), previously prepared by dissolving red HgO (2.0 g) in H_2O (39.5 mL) and conc. H_2SO_4 (10.5 mL). The reaction mixture was stirred for 2 h at room temperature and then the ethanol was removed under reduced pressure. Water was added to the residue and the mixture was extracted with chloroform. The organic extract was dried over $MgSO_4$ and concentrated under reduced pressure. The product was purified by column chromatography eluting with (7:3) hexane-ethyl acetate. Yield 223 mg (0.589 mmol, 71%). IR (neat film) 1740-1710, 730, 690 cm^{-1}; ^{1}H-NMR (CCl_4, 80 M-Hz) δ 1.10-1.40 (6H, dt), 1.70-2.55 (4H, m), 2.60-2.90 (1H, m), 3.60 (2H, s), 3.90-4.40 (5H, m), 4.50 (2H, s), 5.00-5.30 (1H, m), 7.35 (5H, s). ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 14.0 (CH_3), 14.1 (CH_3), 34.8 (CH_2), 38.2 (CH_2), 49.0 (CH_2), 55.7 (CH), 61.3 (CH_2), 64.0 (CH_2), 70.6 (CH_2), 77.7 (CH), 79.2 (CH), 127.5 (CH), 128.3 (CH), 138.1 (C), 154.9 (CO), 166.8 (CO), 202.9 (CO).

*(1S, 2S, 4R)-2-Carbethoxyacetyl-4-benzyloxy-cyclopentyl carbonate (**9b**) and its enantiomer (racemic mixture)*

This compound was prepared in a manner identical with that of **9a**, starting with compound **5b**. Yield 232 mg (0.613 mmol, 74%) IR (neat film) 1750-1710, 735, 698 cm^{-1}, ^{1}H-NMR (CCl_4, 80 MHz) δ 1.10-1.45 (6H, dt), 1.80-2.40 (4H, m), 2.50-2.85 (1H, m), 3.45 (2H, s), 3.95-4.35 (5H, m), 4.40 (2H, s), 4.80-5.30 (1H, m), 7.20 (5H,s).

*(1S, 2S, 4S)-2-Carbethoxyacetyl-4-benzyloxy-cyclopentanol (**9c**) and its enantiomer (racemic mixture)*

The reaction was performed as previously described for the compound **9a,** using compound **8a** (57 mg, 0.157 mmol) in EtOH (1.0 mL) and aqueous solution of 4%$HgSO_4$ (0.5 mL). Yield 46 mg (0.151 mmol, 96 %). ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 1.05-1.40 (3H, t), 1.65-1.80 (4H, m), 2.65 (1H, br.s), 3.10-3.50 (1H, m), 3.55 (2H, s), 3.95-4.40 (4H, m), 4.40 (2H, s), 5.05 (1H, s), 7.30 (5H, s).

*(Z)- and (E)-(1S, 2S, 4S)-2-[1-(1-Piperidinyl)]-carbethoxyethenyl-4-benzyloxy-cyclopentyl carbonate (**10a**) and their enantiomers (racemic mixtures) [9]*

Piperidine (246 mg, 2.89 mmol) was added to a solution of **5a** (517 mg, 1.437 mmol) in anhydrous ether (1.9 mL). The mixture was stirred for 4 h at room temperature. The excess of the reagent and the solvent was removed under reduced pressure and the crude product was isolated as a mixture of *Z* + *E* diastereoisomers. Yield 641 mg (1.44 mmol, 100 %). IR (neat film) 1740, 1690, 1265, 750, 698 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 60 MHz) δ 1.00-1.90 (12H, m), 1.90-2.90 (4H, m), 2.95-3.30 (4H, m), 3.40-3.65 (1H, m), 3.70-4.30 (5H, m), 4.45 (2H, s), 4.60-4.75 (1 H, s), 5.10-5.60 (1H, m), 7.25 (5H, s).

*(Z)-and (E)-(1S, 2S, 4R)-2-[1-(1-Piperidinyl)]-carbethoxyethenyl-4-benzyloxycyclopentyl carbonate (**10b**) and their enantiomers (racemic mixtures)*

These compounds were prepared in a manner identical to that of **10a,** starting with compound **5b,** also resulting in a mixture of *Z* + *E* diastereoisomers. Yield 641 mg (1.44 mmol, 100 %). IR (neat film) 1743, 1692, 1262, 750, 698

cm^{-1}; ^{1}H-NMR (CCl_4, 80MHz) δ 1.05-1.40 (6H, m), 1.40-1.70 (6H, m), 1.70-2.90 (4H, m), 2.90-3.30 (4H, m), 3.40-3.70 (1H, m), 3.75-4.30 (5H, m), 4.45 (2H, d), 4.60, 4.70 (1H, s), 5.10-5.60 (1H, m), 7.20(5H, s).

*2-Carbethoxyacetyl-4-benzyloxy-cyclopentene (**11**)*

The compound **10a** (234 mg, 0.526 mmol) was applied to a silica gel column (15 mL) eluting with $CHCl_3$;. Yield 117 mg (0.406 mmol, 77 %). IR (neat film) 1742, 1653, 735, 698 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 80 MHz) δ 1.10-1.40 (6H, dt), 2.50-2.80 (4H, m), 3.50 (2H, s), 4.00-4.30 (5H, m), 4.45 (2H, d), 4.95 (1 H, s), 6.40-6.70 (1 H, m), 7.25 (5H, s); ^{13}C-NMR ($CDCl_3$, 20 MHz), keto form δ 14.0 (CH_3), 37.3 (CH_2), 41.0 (CH_2), 45.7 (CH_2), 61.0 (CH_2), 70.7 (CH_2), 77.6 (CH), 127.5 (CH), 128.3 (CH), 138.1 (C), 142.6 (CH), 142.7 (C), 167.3 (CO), 190.0 (CO); enol form δ 14.1 (CH_3), 37.7 (CH_2), 40.1 (CH_2), 60.0 (CH_2), 70.7 (CH_2), 78.2 (CH), 88.9 (CH), 127.5 (CH), 128.3 (CH), 134.1 (CH), 135.7 (C), 138.2 (C), 167.6 (CO), 172.8 (CO).

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