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An efficient synthesis of enantiopure (+)- and (−)-3-*exo*-amino-7,7-dimethoxynorbornan-2-*exo*-ols

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Abstract—We describe the synthesis of new amino alcohols (+)- and (−)-3-*exo*-amino-7,7-dimethoxynorbonan-2-*exo*-ols. The (+)- or (−)-7,7-dimethoxy-1,4,5,6-tetrachlorobicyclo[2.2.1]hept-5-en-2-*endo*-ol, obtained from the enzyme catalysed transesterification of the racemate, was reduced and dechlorinated (Na/NH_3; ethanol), followed by pyridinium chlorochromate oxidation of the resultant alcohols to the corresponding ketones. After treatment with *t*-BuOK/BuONO, in a nitrosation reaction, α-keto oximes were obtained. Reduction over two steps with $NaBH_4$ and $NaBH_4/NiCl_2{\cdot}6H_2O$ followed by in situ acetylation furnished the corresponding acetamido esters, which were hydrolysed with CH_3OH/Na to produce the enantiopure amino alcohols in good yields.

1. Introduction

A wide range of 1,2-amino alcohols have been used as chiral building blocks in organic synthesis, as well as chiral auxiliaries or ligands.[1] In many cases, it has been recognised that homochiral amino alcohols are versatile reagents for the generation of enantiopure materials, as examples: the *cis*-1-amino-2-indanol,[2] an important subunit in drug design and the asymmetric synthesis of biologically active molecules, and the optically active 2-amino-1,3,4-butanetriol, a building block for the synthesis of a potent HIV-protease inhibitor.[3] As intermediates, chiral β-amino alcohols were recently used for the stereocontrolled synthesis of tetrahydroisoquinolines, an important class of physiologically active alkaloids.[4] Furthermore, the abundance and crystallinity of (+)-camphor has attracted considerable interest throughout the synthesis of enantiomerically pure derivatives including 3-*endo*-amino-2-*endo*-bornanol,[5] *exo*,*exo*-amino alcohol,[6] *anti*-(+)-camphorquinone-3-oxime[7] and bridgehead-substituted 2-norbonanones and 2-norbonanoximes.[8] Bicyclic amino alcohol derivatives are stereochemically constrained compounds and are interesting systems for use as chiral auxiliaries,[9–13] synthetic intermediates and chiral ligands for asymmetric synthesis.[9,15–17]

A convenient method for obtaining enantiopure materials is enzyme catalysed acylation.[18] The enzyme catalysed transesterification using vinyl acetate[19–21] was applied, in 1990, for the resolution of 7,7-disubstituted 1,4,5,6-tetrachlorobicyclo[2.2.1]hept-5-en-2-ols using lipase from *C. rugosa*.[22]

In recent years, our group has synthesised[23] and studied constrained polycyclic compounds by NMR spectroscopy.[24–27] The enantiomeric analysis of chiral polycyclic derivatives by NMR using a mixture of chiral and achiral shift reagents was reported,[28,29] as well as an approach to determine the optimal position of the lanthanide ion in complexes formed by shift reagents and substrates[30] using the pseudocontact model. Additionally, we reported the kinetic resolution of a very hindered secondary pentacyclic alcohol[31] employing the lipase from *C. rugosa* in vinyl acetate.

In this work, we describe the efficient synthesis of enantiopure (+)- and (−)-3-*exo*-amino-7,7-dimethoxynorbonan-2-*exo*-ols in six steps from (+)- and (−)-7,7-dimethoxy-1,4,5,6-tetrachlorobicyclo[2.2.1]hept-5-en-2-*endo*-ol.

2. Results and discussion

(±) - 7,7 - Dimethoxy - 1,4,5,6 - tetrachlorobicyclo[2.2.1]-hept-5-en-2-*endo*-ol, obtained from the Diels–Alder

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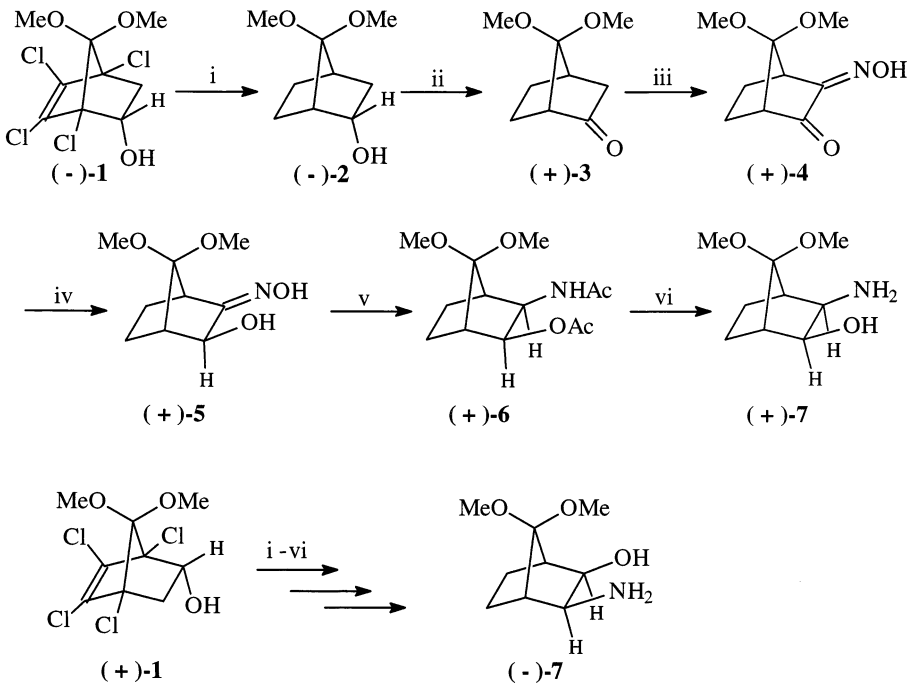
reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and vinyl acetate followed by acid hydrolysis (sulfuric acid/methanol), was subjected to transesterification[22] with vinyl acetate and lipase from *Candida rugosa*, over 7 days. The enantiomeric purity of the products was determined by chiral gas chromatography (alcohol: e.e. 98%; acetate: e.e. 99%). The acetate was hydrolysed (sulfuric acid/methanol) to furnish the corresponding alcohol (+)-**1**. The absolute configuration of each product (−)-**1** and (+)-**1** was assigned as (1*R*,2*S*,4*S*) and (1*S*,2*R*,4*R*), respectively, by comparison of the specific rotation measurements reported by Berger et al.[22] The pure alcohols (−)-**1** and (+)-**1** were then reduced and dechlorinated using the reductive system Na/NH_3 liq./ethanol (Scheme 1) to afford (−)-**2** or (+)-**2**.

The dechlorinated alcohols (−)-**2** or (+)-**2** were oxidised by treatment with pyridinium chlorochromate (PCC)[32] giving the corresponding ketones (+)-**3** and (−)-**3**, respectively. In the Roy camphor nitrosation reaction,[7] the ketones (+)-**3** or (−)-**3** were treated with the *t*-BuOK/BuONO system, furnishing the α-keto oximes (+)-**4** and (−)-**4**, each one, with a diasteriomeric ratio of (*E*)-/(*Z*)-configurations of 4:1.

Despite earlier work reporting the reduction of bicyclic α-keto oxime derivatives to their respective *endo–endo* and *exo–exo* amino alcohols by treatment with $LiAlH_4$ or amino alcohols (*exo–exo*) by reaction with $NaBH_4$,[12–14] followed by hydrogenation with H_2/PtO_2, we observed that these methods were not efficient to reduce the α-keto oxime (+)-**4** or (−)-**4** as stereoisomeric mixtures (*endo–endo*, *endo–exo* and *exo–exo*) were always obtained. Hence, we decided to proceed with the reduction of α-keto oxime (+)-**4** or (−)-**4** in two steps. Firstly, $NaBH_4$ reduction afforded the hydroxy oximes (+)-**5** and (−)-**5**, respectively, and then, in a second step, these oximes were reduced using $NaBH_4/NiCl_2{\cdot}6H_2O$.[6,33] This methodology proved to be efficient in the reduction of the hydroxy oxime (+)-**5** or (−)-**5**. However, direct extraction and purification of product *exo*,*exo*-(+)-**7** or (−)-**7** afforded the amino alcohol in poor yields. To overcome this, an in situ acetylation of (+)-**7** or (−)-**7** was carried out after the hydroxy oxime reduction, producing (+)-**6** or (−)-**6** in good yield and purity (Scheme 1). Finally, the acetamido esters *exo*,*exo*-(+)-**6** or (−)-**6** were treated with Na/MeOH to provide the enantiomerically pure amino alcohols *exo*,*exo*-(+)-**7** or (−)-**7** in high 88% yields.

The *exo*,*exo*-configuration of amino alcohol **7** was assigned by NOESY NMR experiment. The interactions between the α-hydrogen of alcohol and amine groups, at positions 2 and 3, with the hydrogens at positions 5 and 6 of the ring were observed. The chiral gas chromatography analysis has showed that all intermediates as well as the amino alcohols (+)-**7** or (−)-**7** maintained the enantiomeric excess (98 and 99%, respectively) in the course of this synthetic route.

Table 1 shows the specific rotation values of compounds **2**–**7**. For compounds **4** and **5**, these values correspond to the diasteriomeric mixtures of oximes (*E*)/(*Z*) (4:1 and 6:4, respectively).



Scheme 1. (i) Na, NH_3 liq., ethanol; (ii) PCC; (iii) *t*-BuOK, BuONO; (iv) $NaBH_4$, (v) a. $NaBH_4$, $NiCl_2{\cdot}6H_2O$, b. Ac_2O; (vi) Na, MeOH.

Table 1. Specific rotation values of compounds **2**–**7** (ethyl acetate)

Compound	$[\alpha]_D^{20}$	c (g/100 mL)
(−)-**2**	−1	3.07
(+)-**2**	+1	3.07
(−)-**3**	−53	1.88
(+)-**3**	+55	1.88
(−)-**4**	−52[a]	1.00
(+)-**4**	+53[a]	1.00
(−)-**5**	−39[b]	1.52
(+)-**5**	+40[b]	1.52
(−)-**6**	−15	1.04
(+)-**6**	+14	1.04
(−)-**7**	−26	1.04
(+)-**7**	+26	1.04

[a] Ratio (*E*)/(*Z*): 4:1.
[b] Ratio (*E*)/(*Z*): 6:4.

3. Conclusions

In summary, new enantiomerically pure amino alcohols (+)- and (−)-3-*exo*-amino-7,7-dimethoxynorbonan-2-*exo*-ols were easily obtained from dimethoxy-tetrachlorobicyclo[2.2.1]heptenol by simple procedures with good yields. This constitutes an effective and convenient synthetic approach for the preparation of new chiral auxiliaries, synthons and building blocks.

4. Experimental

4.1. General

NMR spectra were recorded on Varian VXR-200 or Inova 300 spectrometers at magnetic fields of 4.7 and 7.05 T at 22°C. Chemical shifts are expressed in δ (ppm) relative to TMS as an internal standard. Infrared spectra were recorded using a FTIR-Mattson 3020 spectrometer. Products were analysed by GC on a SHIMADZU chromatograph model GC-171 and Varian Model star 3400 CX chromatograph both equipped with FID using BETA-DEX™ 120 column (30 m×0.22 mm (i.d.)×1.25 μm). Optical rotations were measured with a Perkin–Elmer polarimeter model 341 with a 1 cm cell at 20°C. HRMS spectra were obtained on a Jeol AX500 spectrometer.

The descriptions of the experimental procedures are the same for synthesis to the respective (±), (−) and (+) products.

4.2. (−)-7,7-Dimethoxynorbornan-2-*endo*-ol (−)-2[32]

A solution of the alcohol (−)-**1**[22] (7.43 g, 24.2 mmol) in dry ethanol (4.2 mL, 71.6 mmol) and dry THF (45 mL) was added in small portions to a solution of sodium (5.12 g, 0.22 mol) in ammonia (230 mL) at −78°C, under vigorous stirring for 0.5 h. Then, the mixture was treated with of saturated aqueous ammonium chloride solution (50 mL). The ammonia was evaporated and the usual ethereal extraction sequence followed to produce 3.0 g (17.4 mmol) of a yellow oil, corresponding to alcohol (−)-**2** (yield: 72%). FTIR (film): ν (cm^{-1}): 3409 (C-OH). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.98 (m, 1H), 1.88 (m, 2H), 2.12 (m, 3H), 3.05 (s, 3H), 3.09 (s, 3H), 4.3 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 17.5 (CH_2), 27.6 (CH_2), 38.4 (CH_2), 38.5 (CH), 43.8 (CH), 50.0 (CH_3), 50.48 (CH_3), 70.1 (CH), 114.1.

4.3. (+)-7,7-Dimethoxynorbornan-2-one (+)-3[32]

The alcohol (−)-**2** (0.31 g, 1.8 mmol) was dissolved in of dry methylene chloride (40 mL) under stirring. To this solution was added small portions of pyridinium chlorochromate (PCC, 775 mg, 3.6 mmol) at 0°C. The suspension was stirred at room temperature for an additional 4 h. Ethyl ether (20 mL) was added and a black precipitate formed, which was filtered off with a small column fitted with silica gel and eluted with ethyl ether. The organic solution was concentrated producing of a yellow oil of the pure ketone (+)-**3** (290 mg, 1.7 mmol, 95%). FTIR (film): ν (cm^{-1}): 1755 (C=O). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.42 (m, 2H), 1.8 (s, 1H), 1.95 (m, 2H), 2.38 (m, 1H), 2.47 (m, 2H), 3.21 (s, 3H), 3.24 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.2 (CH_2), 25.9 (CH_2), 38.1 (CH), 44.0 (CH_2), 49.9 (CH_3), 50.8 (CH_3), 52.6 (CH), 111.5 (C), 212.7 (C).

4.4. (+)-3-Hydroxyimino-7,7-dimethoxynorbornan-2-one (+)-4

A solution of (+)-**3** (400 mg, 2.35 mmol) in dry THF (0.5 mL) was added to a magnetically stirred solution of *t*-BuOK (0.31 g, 2.82 mmol) in dry THF (1.5 mL) at −30°C under an inert gas atmosphere. The mixture was stirred at −30°C for 10 min, treated with BuONO (0.29 g, 2.82 mmol), and stirred at room temperature for 12 h. The solvent was evaporated and the residue was diluted in water (40 mL). The aqueous phase was extracted with ethyl ether (3×30 mL). The aqueous phase was acidified with 5% aqueous HCl (pH 4) and extracted with ethyl ether (3×30 mL). After solvent evaporation, a yellow oil was obtained corresponding to a mixture of the *anti* (80%) and *syn* (20%) forms of the oxime (+)-**4** (yield: 400 mg, 2.01 mmol, 85%). Pure *anti*-oxime was obtained when the mixture was stirred under reflux for several days in ethyl acetate. FTIR (film): ν (cm^{-1}): 3315 (OH), 1748 (C=O), 1644 (C=N). δ ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.63 (m, 2H), 2.09 (m, 2H), 2.88 (m, 1H), 3.22 (s, 3H), 3.27 (s, 3H), 3.78 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.3 (CH_2), 23.5 (CH_2), 41.7 (CH), 49.8 (CH_3), 51.6 (CH_3), 53.2 (CH), 109.5 (C), 157.5 (C=NOH), 198.19 (C=O). HRMS found: m/z 199.0849; calcd for $C_9H_{13}NO_4[M]^+$: 199.0844

4.5. (+)-3-*exo*-Hydroxy-7,7-dimethoxynorbornan-2-one oxime (+)-5

A diastereomeric mixture of the keto oxime (+)-**4** (700 mg, 3.5 mmol) was dissolved in of methanol (20 mL). The solution was cooled at 0°C and small portions powdered sodium borohydride (150 mg, 4.0 mmol) were added with stirring. The solution was warmed up

to room temperature and stirred for an additional 3 h. The solvent was removed using a rotatory evaporator and water (15 mL) was added to the residue. The solution was acidified with HCl 5% (pH 4). Three extractions with chloroform produced of a pale yellow oil (660 mg, 3.28 mmol, 93%) corresponding to a mixture of *anti* (60%) and *syn* (40%) hydroxy oxime (+)-**5**. FTIR (film): ν (cm^{-1}): 3328 (OH), 1643 (C=N). δ ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.31 (m, 2H and 2H), 2.01 (m, 2H and 2H), 2.37 (m, 2H), 2.85 (m, 1H) 3.29 (m, 6H and 6H), 3.54 (m, 1H), 4.11 (s, 1H, *anti*), 4.42 (s, 1H, *syn*), 9.45 (bs, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.4 (CH_2), 22.6 (CH_2), 22.8 (CH_2), 24.4 (CH_2), 40.6 (CH), 44.4 (CH), 44.8 (CH), 50.1 (CH_3), 51.1 (CH_3), 51.2 (CH_3), 72.6 (CH, *syn*), 74.9 (CH, *anti*), 112.8 (C, *syn*), 113.2 (C, *anti*), 164.93 (C=NOH, *anti*), 164.97 (C=NOH, *syn*). HRMS found: m/z 201.0975; calcd for $C_9H_{15}NO_4$[M]$^+$: 201.1001

4.6. (+)-3-*exo*-Acetamido-7,7-dimethoxynorbornan-2-exo-yl acetate (+)-6

To a solution of hydroxy oxime (+)-**5** (540 mg, 2.86 mmol) in methanol (40 mL), nickel(II) chloride hexahydrate (1.2 g, 5.04 mmol) was added under magnetic stirring. After nickel dissolution, the solution was cooled to −78°C. Powdered sodium borohydride (1.0 g, 26.2 mmol) was added in small portions under efficient stirring. The solution turned blue, and was stirred for an additional 12 h when the colour changed to black. The methanol was removed and acetic anhydride (30 mL) was added and the solution refluxed for 90 min. The anhydride excess was removed by distillation. The residue was neutralised with a solution of saturated potassium carbonate and extracted three times with chloroform, yielding, after solvent evaporation, a pale yellow solid corresponding to the compound (+)-**6** (700 mg, 2.58 mmol, 95%). Mp 142–143°C. FTIR (KBr): ν (cm^{-1}): 3312 (NH), 1731 (C=O), 1660 (C=O amide). δ ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.29 (m, 2H), 1.75 (m, 1H), 1.9 (m, 1H), 1.97 (s, 3H), 2.08 (s, 3H), 2.24 (m, 2H), 3.25 (s, 3H), 3.30 (s, 3H), 4.41 (dd, J=9.9 Hz, 8.1 Hz, 1H), 4.81 (d, J=8.1 Hz, 1H), 6.38 (d, J=9.9 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.6 (CH_3), 23.2 (CH_3), 23.4 (CH_2), 23.5 (CH_3), 42.1 (CH), 43.2 (CH), 50.2 (CH_3), 50.9 (CH_3), 53.1 (CH), 75.0 (CH), 114.3 (C), 168.9 (C=O), 169.4 (C=O). HRMS found: m/z 272.1521; calcd for $C_{13}H_{22}NO_5$[M]$^+$: 272.1498

4.7. (+)-3-*exo*-Amino-7,7-dimethoxynorbornan-2-*exo*-ol (+)-7

To a solution of (+)-**6** (700 mg, 2.58 mmol) in methanol (15 mL), small portions of sodium (900 mg, 39 mmol) were added under an inert atmosphere and magnetic stirring. The reaction was refluxed for 6 h. The methanol was evaporated and water (50 mL) was added. Four extractions with chloroform produced 430 mg (2.29 mmol) of a yellow oil corresponding to amino alcohol (−)-**7** (yield: 88%). Mp 67–68°C. FTIR (KBr): ν (cm^{-1}): 3344 and 3289 (NH_2), 3328 (OH). δ ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.1 (m, 2H), 1.75 (m, 2H), 1.95 (m, 1H), 2.15 (m, 1H), 3.09 (d, J=7.5 Hz, 1H), 3.23 (s, 3H), 3.31 (s, 3H), 3.63 (d, J=7.5 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 23.3 (CH_2), 24.7 (CH_2), 43.7 (CH), 44.9 (CH), 49.9 (CH_3), 51.2 (CH_3), 56.9 (CH), 73.9 (CH), 114.6 (C). HRMS found: m/z 188.1276; calcd for $C_9H_8NO_3$ [M]$^+$: 188.1287.

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