ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 2, pp. 282–287. © Pleiades Publishing, Ltd., 2008.
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Preparation of Enantiomeric Pure (–)-(3*R*,4*S*)-1-Benzyl-3,4-epoxypiperidine and Enriched (–)-(*R*)-1-Benzyl-3-hydroxy-1,2,3,6-tetrahydropyridine by Kinetic Separation of (±)-1- Benzyl-3,4-epoxypiperidine under the Action of Chiral Lithium Amides

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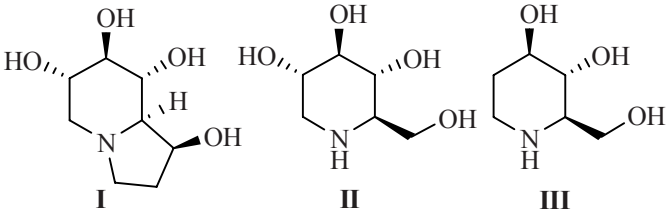
Received June 1, 2007

Abstract—Enantiomeric pure (–)-(3*R*,4*S*)-1-benzyl-3,4-epoxypiperidine and (–)-(*R*)-1-benzyl-3-hydroxy-1,2,3,6-tetrahydropyridine with enantiomeric excess 61.9% were obtained by kinetic separation of (±)-1-benzyl-3,4-epoxypiperidine under the action of lithium salt (+)-(*S*)-2-[(pyrrolidin-1-yl)methyl]pyrrolidine. The sterical direction of the kinetic separation of (±)-1-benzyl-3,4-epoxypiperidine and absolute configurations of the target products were established.

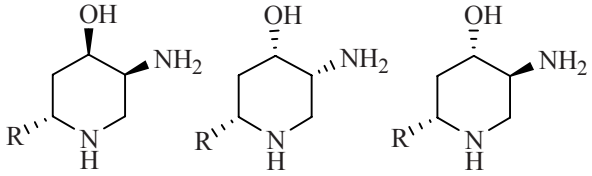
DOI: 10.1134/S1070428008020164

Recently the interest grew significantly to hydroxylated and aminohydroxylated piperidine derivatives, analogs of polyhydroxylated piperidine alkaloids of castanospermine (**I**) family, deoxynojirimycin (**II**), fagomine (**III**) [1, 2], and separated from sea organisms aminohydroxylated alkaloids pseudodistomines A–F **IV–IX** [3–5], glucosidase inhibitors containing a hydroxy- and aminohydroxypiperidine fragment (Scheme 1).

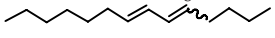
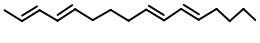
Scheme 1.



I **II** **III**

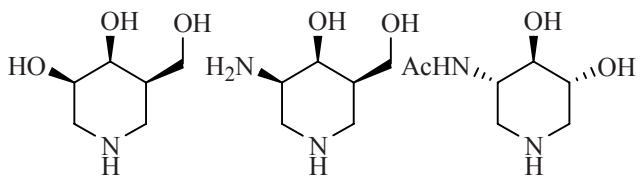


IV–VI **VII, VIII** **IX**

R = R^1,8-*cis* (**IV**), R^1,8-*trans* (**V, VIII, IX**); R = R^2 (**VI, VII**); R^1 =  , R^2 =  .

Both subfamilies of hydroxylated alkaloids or iminosugars are strong inhibitors of a series of glucosidases and related enzymes, they exhibit anticancer and antiviral, in particular, anti-AIDS activity. The presence of an amino group results in a selective inhibition of definite types of glucosidases and hexaminidases. For instance, aminodiol **XI**, aminoanalog of galactoisofagomine (**X**), an inhibitor of β-galactosidase, exhibits a selective inhibiting activity toward β-glucosidase [6]. Acetylamino derivative of 1- deoxynojirimycin (**XII**) inhibits selectively only the β-*N*-acetylglucaminidase [7].

Nowadays an intensive development continues of efficient synthetic procedures for analogs of natural iminosugars [8, 9], and the most promising way is the



X **XI** **XII**

preparation of optically pure synthetic hydroxylated piperidines due to the opportunity of multifold increasing various inhibiting activity of individual enantiomers [10].

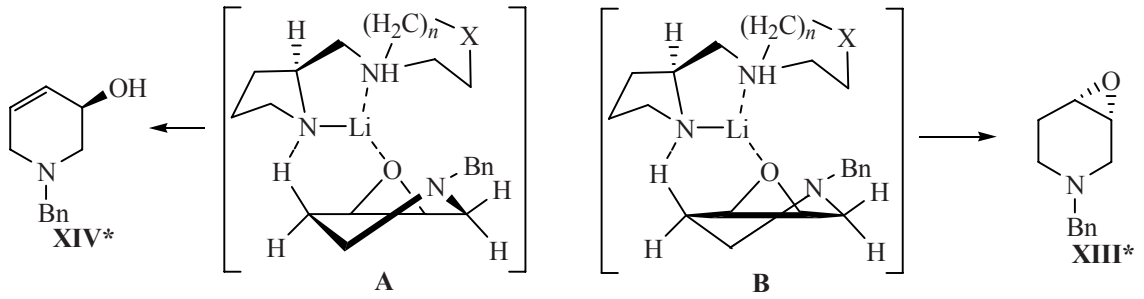
We report here on developing a convenient and efficient synthesis of precursors of versatile optically active 4-amino-3-hydroxylated piperidines while selecting as a case in point optically pure 1-benzyl-3,4-epoxypiperidine and enantiomer-enriched 1-benzyl-3-hydroxy-1,2,3,6-tetrahydropyridine obtained by kinetic separation of (±)-1-benzyl-3,4- epoxypiperidine under the action of chiral lithium amides. We had showed formerly [11] that a series of C- and N-substituted (±)-3,4-epoxypiperidines by the treatment of lithium dialkylamines had been cleanly rearranged into the corresponding (±)-3-hydroxy-1,2,3,6-tetrahydropyridines, therefore in this study we used (±)-1-benzyl-3,4-epoxypiperidine (**XIII**) and (±)-1-benzyl-3-hydroxy-1,2,3,6-tetrahydropyridine (**XIV**) as reference compounds.

It is presumable that in the kinetic separation of (±)-1-benzyl-3,4-epoxypiperidine (**XIII**) by the treatment with chiral lithium amides both enantiomers of epoxide **XIII** in the chiral environment form diastereomer complexes **A** and **B** (Scheme 2) with a different reactivity. Therefore in the course of the rearrangement the synchronous transfer of the *syn*-proton to nitrogen atom and of lithium ion to oxygen in the diastereomer complexes **A** and **B** would occur with a different rate, and the more reactive complex **A** would provide the enantiomer enriched allyl alcohol **XIV***, and the initial enantiomer enriched epoxide **XIII*** would accumulate in the reaction mixture (Scheme 2).

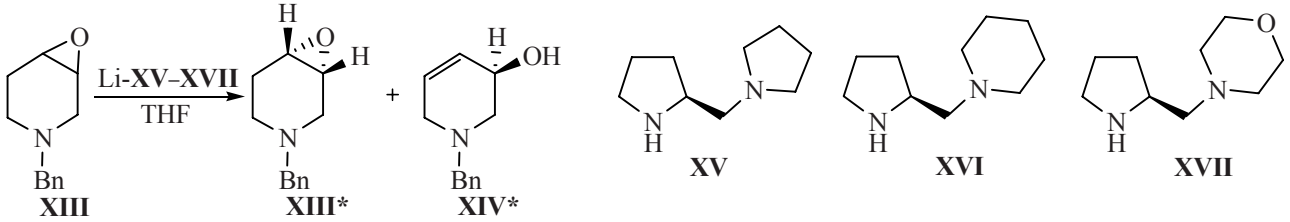
The kinetic separation of (±)-1-benzyl-3,4-epoxypiperidine was performed applying chiral lithium amides based on (+)-(*S*)-2-[(pyrrolidin-1-yl)methyl]pyrrolidine (**XV**), (+)-(*S*)-2-[(piperidin-1-yl)methyl]pyrrolidine (**XVI**), and (+)-(*S*)-2-[(morpholin-1-yl)methyl]pyrrolidine (**XVII**) [12] formerly marked as fairly efficient bases in asymmetrical transformation of *meso*-epoxides and in kinetic separation of racemic epoxides [13–15] (Scheme 3).

We established by chromatographic monitoring the operating temperature range for the kinetic separation of epoxide **XIII** (1.00 equiv) at the action of lithium (+)-(*S*)-2-[(pyrrolidin-1-yl)methyl]pyrrolidinide (Li-**XV**) (0.20 equiv) in THF under an argon atmosphere: At –70°C only the presence of initial (±)-epoxide **XIII** was observed; gradual raising of the temperature of the reaction mixture by 20°C steps and keeping at this temperature for 40 min showed that the rearrangement giving allyl alcohol **XIV*** started in the range –15ч–10°C. The invariability of the mixture with respect to chromatographic analysis was attained by its maintaining at 5°C for 12 h. Further the reaction mixture was hydrolyzed with a saturated ammonium chloride solution till pH 9. The target epoxide **XIII*** and allyl alcohol **XIV*** were extracted with dichloromethane, and

Scheme 2.



Scheme 3.



therewith the chiral amine **XV** remained practically completely in the water phase and therefore was recovered. The GC-MS analysis of the organic phase showed the presence of epoxide **XIII***, allyl alcohol **XIV***, and 4% of chiral amine **XV**. From the water phase at pH 14 75% of amine **XV** was recovered and used in repeated experiments.

The ratio epoxide **XIII*** –allyl alcohol **XIV*** in the reaction mixture according to ^{1}H NMR spectrum was 5.25:1 measured by comparing the integral intensity of the signals of benzyl protons of the epoxide (δ 3.44 ppm) and allyl alcohol (δ 3.58 ppm) and corresponded to the conversion of 16% (ω). In approximately the same weight ratio (5.27:1) in overall yield 94% the chemically individual epoxide **XIII*** and allyl alcohol **XIV*** were isolated by column chromatography on silica gel. The epoxide **XIII*** and allyl alcohol **XIV*** obtained by the kinetic separation of 1 equiv of racemic epoxide **XIII** by the treatment with 0.20 equiv of amide Li-(**XV**) exhibited a specific rotation $[\alpha]_D^{20}$ –0.52 and –52.9° respectively (see the table, run no. *1*).

Applying HPLC on columns with chiral phases we established the enantiomeric excess (*e.e.*) of epoxide **XIII*** with $[\alpha]_D^{20}$ –3.87° equal 83.1% (see the table, run no. *4*) and *e.e.* of allyl alcohol **XIV*** with $[\alpha]_D^{20}$ –52.9° equal 59.8%, (see the table, run no. *1*). The specific rotations for the optically pure epoxide [(–)-**XIII***] and alcohol [(–)-**XIV***] calculated from these data amounted to –88.5 and –4.66° respectively. In further experiments we estimated the *e.e.* values of the target compounds applying these reference figures.

To raise the efficiency of the kinetic separation we carried out a series of experiments varying the amount of amide Li-(**XV**) used with 1 equiv of (±)-epoxide **XIII**. Some of the most important results are presented in the table (runs nos. *2–4*). At increasing the molar fraction of amide Li-(**XV**) as expected grew the *e.e.* of epoxide **XIII*** and decreased the *e.e.* of allyl alcohol **XIV***. At the use of 0.80 equiv of amide Li-(**XV**) and the conversion 75% the *e.e.* values of epoxide **XIII*** and alcohol **XIV*** were 83.1 and 28.1% respectively (see the table, run no. *4*). A considerable effect of supplemental coordination was attained by addition of DBU (see the table, runs nos. *5–7*): At applying equivalent amounts of DBU and amide Li-(**XV**) the *e.e.* of alcohol **XIV*** grew to 61.9 %. Even at ω 31% (see the table, run no. 5) the *e.e.* of allyl alcohol **XIV*** proved to exceed by 2% the value obtained without DBU addition at ω 16% (see the table, run no. *1*). Optically pure epoxide **XIII***, *e.e.* 98.7%, was obtained at the use of 0.95 equiv of Li-(**XV**) and 0.95 equiv of DBU (щ 84%) (see the table, run no. *7*). The kinetic separation of (±)-epoxide **XIII** applying lithium salts of diamines **XVI** and **XVII** turned out to be less efficient and resulted in lower *e.e.* values of target compounds **XIII*** and **XIV*** (see the table, runs nos. *8–11*). In all experiments chiral diamines **XV–XVII** were recovered for repeated use.

Kinetic separation of 1 equiv of (±)-epoxide **XIII** under the action of chiral lithium amides Li-(**XV–XVII**)

Run no.	Li (equiv)/ Amine (equiv)	ω, %[a]	Epoxide (–)-(3*R*,4*S*)-(XIII*)			Alcohol (–)-(3*R*)-(XIV*)		
			$[\alpha]_D^{20}$ ($CHCl_3$), deg	*e.e.*, %	Yield, %	$[\alpha]_D^{20}$ ($CHCl_3$), deg	*e.e.*, %	Yield, %
1	XV (0.20)/(0.00)	16	(–)-0.52	11.1	79	(–)-52.9	59.8	15
2	XV (0.40)/(0.00)	34	(–)-1.34	28.2	61	(–)-49.9	56.4	31
3	XV (0.60)/(0.00)	51	(–)-2.28	48.9	44	(–)-42.9	48.5	45
4	XV (0.80)/(0.00)	75	(–)-3.87	83.1	23	(–)-24.9	28.1	68
5	XV (0.40)/(0.40)	31	(–)-1.26	27.0	62	(–)-54.8	61.9	27
6	XV (0.80)/(0.80)	70	(–)-3.84	82.4	27	(–)-32.2	36.4	60
7	XV (0.95)/(0.95)	84	(–)-4.60	98.7	14	(–)-16.2	18.3	73
8	XVI (0.25)/(0.25)	21	(–)-0.62	13.3	74	(–)-44.8	50.7	19
9	XVI (0.70)/(0.70)	50	(–)-1.91	41.0	45	(–)-37.3	42.1	46
10	XVII (0.25)/(0.25)	20	(–)-0.51	10.9	69	(–)-38.5	43.5	17
11	XVII (0.70)/(0.70)	63	(–)-1.73	37.2	34	(–)-19.3	21.2	58

[a] Conversion ω was estimated from the ratio of integral intensities of the benzyl protons signal of allyl alcohol **XIV*** and epoxide **XIII*** in the ^{1}H NMR spectrum of the reaction mixture.

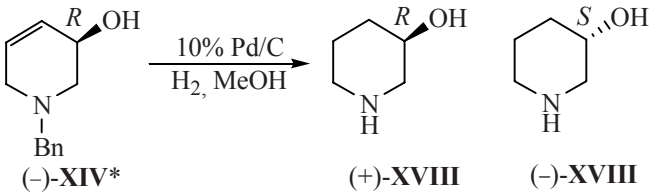
To establish the sterical direction of the kinetic separation of (±)-epoxide **XIII** it was necessary to determine the absolute configuration of allyl alcohol **XIV***. To this end we obtained from allyl alcohol **XIV***, $[\alpha]_D^{20}$ –49.9° (*e.e.* 56.4 %), in 92% yield (+)-enantiomer of 3-hydroxypiperidine [(+)-(**XVIII**)], $[\alpha]_D^{20}$ +4.2°, by means of removing 1-benzyl group by hydrogenolysis on palladium on carbon. The stereochemical comparison of the sign and the value of specific rotation of (+)-3-hydroxypiperidine we obtained with the (–)-enantiomer of (*S*)-3-hydroxypiperidine [(–)-(**XVIII**)] described in [16] led to the conclusion that 3-hydroxypiperidine [(+)-(**XVIII**)] possessed *R*-configuration. The hydrogenation of (–)-allyl alcohol **XIV*** did not affect the stereocenter at C^3 of the piperidine ring, consequently, (–)-allyl alcohol **XIV*** also possessed the *R*-configuration (Scheme 4).

These data make evident the sterical direction of the kinetic separation:

(–)-(*R*)-enantiomer of allyl alcohol [(*R*)-(**XIV***)] forms from (3*S*,4*R*)-enantiomer of epoxide **XIII*,** and less reactive (–)-(3*R*,4*S*)-enantiomer of epoxide **XIII*** accumulates in the reaction mixture; consequently, (–)-1-benzyl-3,4epoxypiperidine [(–)-(**XIII***)] has (3*R*,4*S*)-configuration (Scheme 5).

Hence an economically feasible method of preparation of enantiomeric pure epoxide [(–)-(3*R*, 4*S*)-(**XIII***)], *e.e.* 98.6 %, and enantiomer-enriched allyl alcohol [(–)-(*R*)-(**XIV***)], *e.e.* up to 61.9%, was developed consisting in kinetic separation of (±)-1-benzyl-3,4-epoxypiperidine by treatment with the most efficient chiral lithium amide Li-(**XV**). Both enantiomeric pure epoxide **XIII*** and enantiomer-enriched allyl alcohol **XIV*** are promising chiral precursors for preparation of 3,4-aminoalcohols of the piperidine series, analogs of pseudodistomine alkaloids A–F and other natural iminosugars.

Scheme 4.



EXPRIMENTAL

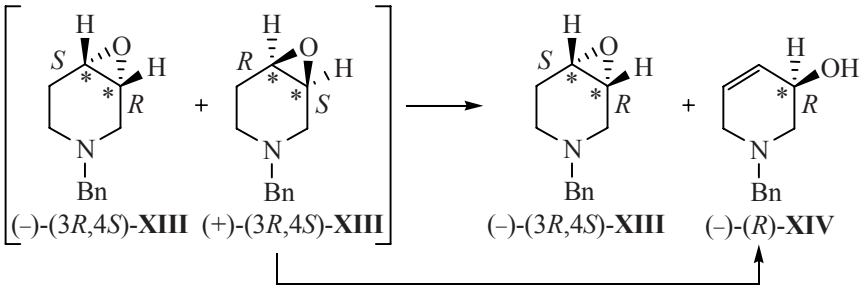
NMR spectra were registered on a spectrometer Varian VXR-400 at operating frequancy 400MHz, internal reference TMS in $CDCl_3$. GC-MS measurements were performed on a Finnigan SSQ7000 instrument, electron impact, 70 eV, column DB5 25 m. TLC was performed on Silufol plates (Merck, Germany). Column chromatography was carried out on a column packed by wet procedure with SiliCagel 60-40 (Merck, Germany). The specific rotation was measured on a polarimeter Perkin-Elmer 241; cell *V* 1 ml, *l* 10 cm.

For separation of enantiomers of epoxide **XIII*** and allyl alcohol **XIV*** a series of chiral columns for HPLC was tested in combination with various eluents. Finally the estimation of the enantiomeric purity of epoxide **XIII*** was carried out on a column Chiracel OJ-H (0.46 × 25 cm), *e.e.* of allyl alcohol **XIV***, on a column Chiracel OD-H (0.46 × 25 cm), eluent hexane–2-propanol, 9:1, 1 ml/min, detector UV, 254 nm.

Synteses of (+)-(*S*)-2-[(pyrrolidine-1-yl)methyl]-pyrrolidine (**XV**), $[\alpha]_D^{20}$ +7.2° (*C* 0.18, C_2H_5OH), (+)-(*S*)-2-[(piperidin-1-yl)methyl]pyrrolidine (**XVI**), $[\alpha]_D^{23}$ +17.9° (*C* 5.00, C_2H_5OH), and (+)-(*S*)-2-[(morpholin-4-yl)methyl]pyrrolidine (**XVII**), $[\alpha]_D^{23}$ +17.6° (without solvent) were carried out as in [12].

Standard procedure of kinetic separation (see the table, run no. *1*). Into a round-bottom flask of 25 ml capacity equipped with a magnetic stirrer and septum

Scheme 5.



was charged under an argon atmosphere 0.250 g (1.60 mmol) of (*S*)-(+)-2-[(1-pyrrolidyl)methyl]pyrrolidine (**XV**) in 12 ml of anhydrous THF. The mixture was cooled to–20°C, and 1.0 ml (1.60 mmol) of 1.6 M *n*-butyllithium solution in hexane was added, and the mixture was stirred for 40 min at –10°C, then the temperature was lowered to –70°C, and 1.510 g (8.00 mmol) of 1-benzyl-3,4-epoxypiperidine (**XIII**) in 4 ml of anhydrous THF was added. The reaction mixture was warmed to 5°C within 3 h and it was left standing at this temperature for 12 h. Then the reaction mixture was cooled to –10°C, was treated with a saturated ammonium chloride solution (5 ml) till pH 9, and extracted with dichloromethane (5× 10 ml). The combined organic extracts were dried with sodium sulfate, the solvent was removed on a rotary evaporator, the crude reaction product (1.50 g) was applied to a column packed with silica gel (20 g) in hexane, gradient elution with a system hexane–ethyl acetate, the content of ethyl acetate from 0 to 25%. The chromatographically uniform fractions were combined.

(–)-(3*R*,4*S*)-1-Benzyl-3,4-epoxypiperidine (XIII*). Yield 1.19 g (79%), $[\alpha]_D^{20}$ –0.52° (C 0.20, $CHCl_3$), *e.e.* 11.1%. Spectral characteristics identical to those of racemic 1-benzyl-3,4-epoxypiperidine (**XIII**) [11]. Colorless oily substance, R_f 0.7 [Silufol (Merck), hexane–acetone, 5:1]. Mass spectrum (electron impact, 70 eV), m/z (I_{rel}, %): 189 $[M]^{+\cdot}$ (17), 188 (5), 172 (4), 160 (2), 146 (2), 133 (19), 132 (10), 118 (3), 112 (4), 104 (3), 98 (15), 92 (13), 91 (100). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.99 m (1H, H^{5a}, $^2J_{5a,5e}$ 14.6, $^3J_{5a,6a}$ 9.4, $^3J_{5a,6e}$ 5.5, $^3J_{5a,4}$ 2.6 Hz), 2.03 d.d.t (1H, H^{5e}, $^2J_{5e,5a}$ 14.6, $^3J_{5e,6a}$ 4.4, $^3J_{5e,6e}$ 4.4, $^3J_{5\varepsilon,4}$ 1.5 Hz), 2.19 d.d.d (1H, H^{6a}, $^2J_{6a,6e}$ 11.8, $^3J_{6a,5a}$ 9.2, $^3J_{6a,5e}$ 4.4 Hz), 2.32 m (1H, H^{6e}, $^2J_{6e,6a}$ 11.8, $^3J_{6e,5a}$ 5.8, $^3J_{6e,5e}$ 4.2, $^4J_{6e,2e}$ 1.2 Hz), 2.67 d (1H, H^{2a}, $^2J_{2a,2e}$ 13.5 Hz), 3.01 d.d.d (1H, H^{2e}, $^2J_{2e,2a}$ 13.5, $^3J_{2e,3}$ 4.1, $^4J_{2e,6e}$ 1.5 Hz), 3.18–3.23 m (2H, H^3, H^4), 3.44 s (2H, $PhCH_2$), 7.21–7.32 m (5H, Ph). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 25.51 (C^5), 45.71, 50.54, 51.19, 52.25, 62.24 (C^2, C^3, C^4, C^6, $PhCH_2$), 127.00, 128.14 (2C), 128.92 (2C), 137.88 (Ar-C).

(–)-(R)-1-Benzyl-3-hydroxy-1,2,3,5-tetrahydropyridine (XIV*). Yield 0.23 g (15%), $[\alpha]_D^{20}$ –52.9° (C 0.27, $CHCl_3$), *e.e.* 59.8%. Spectral characteristics identical to those of (±)-1-benzyl-3-hydroxy-1,2,3,5-tetrahydropyridine (**XIV**) [11]. Colorless oily substance, R_f 0.4 [Silufol (Merck), hexane–acetone, 5:1]. IR spectrum (thin film), ν, cm^{-1}: 1660 (C=C), 3410 (OH bound). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 2.53 d.d.d (1H, H^2, $^2J_{2,2'}$ 11.4, $^3J_{2,3}$ 3.6, *J* 0.6 Hz), 2.71 d.d (1H, $H^{2'}$, $^2J_{2',2}$ 11.4, $^3J_{2',3}$ 3.8 Hz), 2.76 m (1H, H^6, $^2J_{6,6'}$ 16.7 Hz), 2.93 br.s (1H, OH), 3.05 m (1H, $H^{6'}$, $^2J_{6',6}$ 16.7 Hz), 3.59 d (1H, $PhCH_2$, ^2J 13.2 Hz), 3.57 d (1H, $PhCH_2$, ^2J 13.2 Hz), 4.05 m (1H, H^3), 5.76 m (1H, H^5, $^3J_{5,4}$ 10.0 Hz), 5.85 m (1H, H^4, $^3J_{4,5}$ 10.0 Hz), 7.21–7.33 m (5H, Ph). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 52.43, 57.49, 62.31 (C^2, C^6, $PhCH_2$), 64.37 (C^3), 127.93, 128.25 (C^4, C^5), 127.11, 128.16 (2C), 128.99 (2C), 137.47 (Ph).

(+)-(*R*)-3-Hydroxypiperidine (XVIII). In a round-bottom flask of 25 ml capacity equipped with a magnetic stirrer and adapter for hydrogen input 0.530 g (2.80 mmol) of (–)-1-benzyl-3-hydroxy-1,2,3,6-tetrahydropyridine ($[\alpha]_D^{20}$ –49.9°, *e.e.* 56.4%) in 25 ml of MeOH was subjected to hydrogenation in the presence of 0.050 g (10%) of Pd/C at room temperature while vigorous stirring for 15 h. The completion of the process was monitored by TLC. The catalyst was filtered off, the solvent was evaporated. Yield 0.260 g (92%) of chromatographically individual compound [(+)-(**XVIII**)], viscous oily substance, R_f 0.1 (Silufol, hexane–acetone, 2:1). Cromato-mass spectrum, *m/z* (I_{rel}, %): 101 (3) $[M]^{+\cdot}$. $C_5H_{11}NO$. M_{calc} 101. Chemical purity 97%, $[\alpha]_D^{20}$ +4.2° (C 0.8, MeOH). For (–)-(*S*)-enantiomer **XVIII** $[\alpha]_D^{20}$ –7.5° (C 2, MeOH) [16].

The study was carried out under a financial support of the Russian Foundation for Basic Research (grant no. 05-03-32658a).

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