Russian Journal of Organic Chemistry, Vol. 38, No. 1, 2002, pp. 104–110. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 1, 2002, pp. 112–117.

Dedicated to Full Member of the Russian Academy of Sciences M.G. Voronkov on the 80th Anniversary of His Birth

Diamines Having a C_2 Symmetry. Synthesis and Application as Ligands in the Hydrogenation of Prochiral Substrates over Rhodium Complexes*

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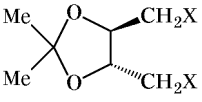
Received April 18, 2001

Abstract—Chiral diamines having a C_2 symmetry, (4*S*,5*S*)-2,2-dimethyl-4,5-bis(aminomethyl)-1,3-dioxolane and (5*S*,5′*S*)-2,2,2′,2′-tetramethyl-3,3′-diphenyl-5,5′-bioxazolidine, were synthesized on the basis of (+)-(2*R*,3*R*)-tartaric acid. Their structure was proved by X-ray analysis. The products were used as ligands in rhodium catalyst for enantioselective hydrogenation of α-acetamidocinnamic and itaconic acids.

2,3-*O*-Isopropylidenedioxy-1,4-bis(diphenylphosphino)butane (DIOP, **Ia**) is widely used as chelating bis-phosphine ligand in catalysts for asymmetric hydrogenation [1–6]. Bis-phosphine rhodium(I) complexes are highly efficient stereo- and enantioselective catalysts for transformations of unsaturated compounds. On the other hand, they are characterized by increased sensitivity to moisture and oxygen. Therefore, apart from bis-phosphine ligands, other conformationally stable compounds, in particular N,N-bidentate ones which are more resistant to oxidation, attract researchers' attention.



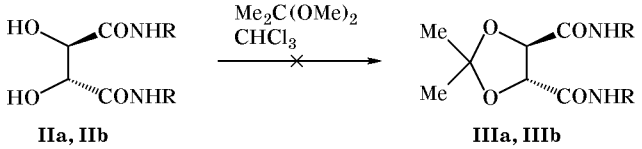
Ia–Id

X = PPh_2 (**a**), NMe_2 (**b**), NH_2 (**c**), NHPh (**d**).

Nitrogen analogs of DIOP, namely optically active diamines like **I** (X = NH_2, NR_2), are known as ligands for chiral catalysts which are used for preparation of polymers with a high degree of spirality [7], as well as ligands for synthesis of platinum(II) complexes which exhibit antitumor activity [8, 9]. We previously studied hydrogenation with molecular hydrogen of prochiral unsaturated carboxylic acids over rhodium catalyst containing ligand **Ib**; as a result, optical yields of up to 30% were obtained. We have found that enhanced stereogeneity of the nitrogen in diamine ligands is necessary to raise the optical yield of hydrogenation products [10–12]. In continuation of our studies on the properties of catalysts for chiral hydrogenation on the basis of nitrogen analogs of DIOP, we have synthesized new chelating diamine ligands and examined the efficiency of some rhodium complexes derived therefrom *in situ* in the hydrogenation of unsaturated prochiral carboxylic acids.

The scheme used previously [13] for preparation of diamine **Ib** includes aminolysis of diethyl tartrate and subsequent cyclization by the action of dimethoxypropane and reduction (Scheme 1). However, we failed to obtain the desired products by this procedure,

Scheme 1.



IIa, IIb **IIIa, IIIb**

R = H (**a**), Ph (**b**).

* This study was financially supported by the Russian Foundation for Basic Research (project no. 00-03-32578).

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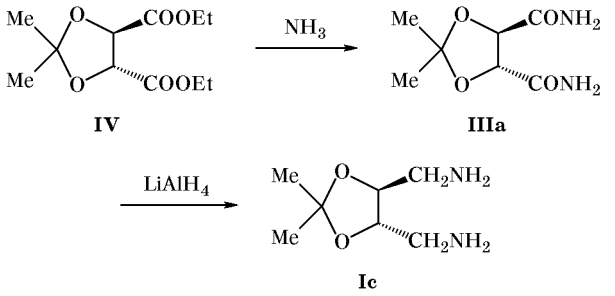
presumably because of the poor solubility of amides **IIa** and **IIb** in chloroform.

A fairly laborious procedure for preparation of compound **Ic** and its analogs with various substituents in position *2* of the dioxolane ring was described in [8]. It consists of cyclization of threitol 1,4-bis-(methanesulfonate) to 1,3-dioxolane-4,5-diyl bis-(methanesulfonate) (**I**, X = OSO_2CH_3), followed by treatment with sodium azide and reduction of diazide **I** (X = N_3). We synthesized ligand **Ic** by a simpler alternative procedure shown in Scheme 2.

Scheme 2.

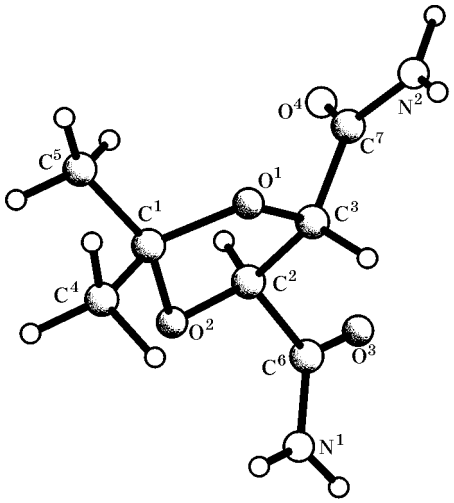


The structure of intermediate diamide **IIIa** was proved by X-ray analysis. The dioxolane ring in molecule **IIIa** (Table 1) has a clearly defined *envelope* conformation with the O^2 atom deviating by 0.51 Å from the plane formed by the four remaining atoms (which are coplanar within 0.01 Å). Compound **IIIa** in crystal gives rise to a three-dimensional network of intermolecular hydrogen bonds N–H···O involving the amide groups (Table 2).

Unlike ammonia, the reaction of less basic aniline with diethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (**IV**) does not give the desired aminolysis product. When the reaction of diester **IV** with aniline was performed under severe conditions (at elevated temperature in the presence of sodium methoxide), we obtained an unexpected product, *N,N′*-diphenyloxamide, whose structure was confirmed by the ^1H and ^{13}C NMR spectra and elemental analysis (its melting point coincided with that reported in the literature). This product is likely to be formed as a result of elimination of acetone with opening of the dioxolane ring, followed by rearrangment and aminolysis (Scheme 3). The proposed scheme is supported by identification of volatile products, acetone, ethanol, and ethyl acetate, which were isolated from the reaction mixture by distillation and were identified by GLC and ^1H NMR spectroscopy.

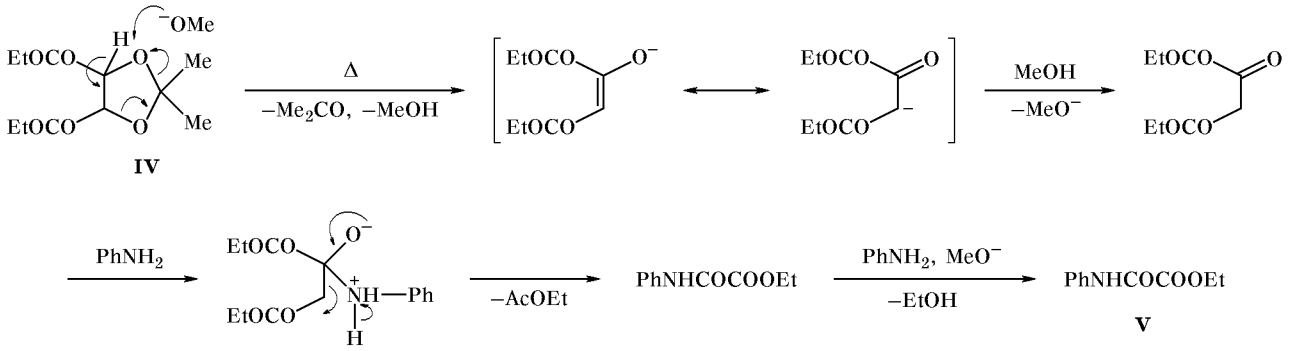
Our attempt to synthesize diamine **Id** by reduction of diamide **IIb**, which was in turn prepared from diethyl tartrate and aniline, and subsequent cyclization according to Scheme 4 unexpectedly resulted in formation of (5*S*,5′*S*)-2,2,2′,2′-tetramethyl-3,3′-diphenyl-5,5′-bioxazolidine (**VII**). The structure of product **VII** was confirmed by the ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum contains signals from aromatic protons and CH, CH_2, and CH_3 groups at a ratio of 5:1:2:6 rather than 5:1:2:3 as might be expected for structure **Id**. Diastereotopic CH_3 groups

Table 1. Bond lengths *d* and bond angles ω in the molecule of (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxamide (**IIIa**)



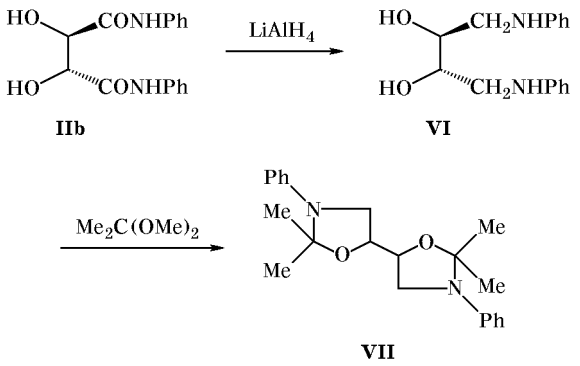
Bond	*d*, Å	Bond	*d*, Å
$O^1–C^3$	1.409 (3)	$N^2–C^7$	1.306 (3)
$O^1–C^1$	1.428 (3)	$C^1–C^4$	1.499 (4)
$O^2–C^1$	1.428 (3)	$C^1–C^5$	1.503 (5)
$O^2–C^2$	1.430 (3)	$C^2–C^6$	1.505 (3)
$O^3–C^6$	1.230 (3)	$C^2–C^3$	1.535 (3)
$O^4–C^7$	1.230 (3)	$C^3–C^7$	1.520 (3)
$N^1–C^6$	1.318 (3)		
Angle	**ω, deg**	**Angle**	**ω, deg**
$C^3O^1C^1$	109.47 (15)	$C^6C^2C^3$	110.99 (18)
$C^1O^2C^2$	105.83 (16)	$O^1C^3C^7$	110.5 (2)
$O^2C^1O^1$	104.08 (17)	$O^1C^3C^2$	104.69 (16)
$O^2C^1C^4$	109.1 (2)	$C^7C^3C^2$	114.9 (2)
$O^1C^1C^4$	107.5 (2)	$O^3C^6N^1$	123.4 (2)
$O^2C^1C^5$	110.5 (3)	$O^3C^6C^2$	117.96 (18)
$O^1C^1C^5$	111.4 (3)	$N^1C^6C^2$	118.5 (2)
$C^4C^1C^5$	113.9 (3)	$O^4C^7N^2$	124.18 (19)
$O^2C^2C^6$	112.48 (17)	$O^4C^7C^3$	121.1 (2)
$O^2C^2C^3$	102.64 (17)	$N^2C^7C^3$	114.7 (2)

Scheme 3.



appear in the spectrum of **VII** in $CDCl_3$ as two singlets, whereas in C_6D_6 only one singlet is observed. The structure of compound **VII** was unambiguously established by X-ray analysis. The geometric parameters of molecule **VII** are collected in Table 3.

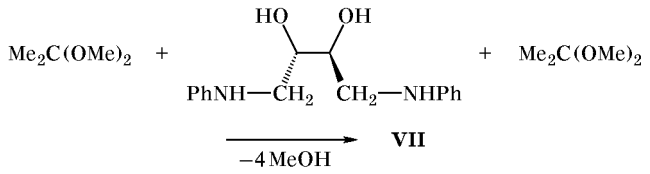
Scheme 4.



A unit cell of compound **VII** in crystal contains two symmetry-independent molecules each having its own C_2 pseudosymmetry. The two molecules are interrelated through a noncrystallographic inversion center at the point [[1/4,3/4,1/4]]. The conformations of these molecules differ mainly by the angle formed by the phenyl group and mean-square plane of the neighboring heteroring. The tetrahydrooxazole rings adopt a clearly defined *envelope* conformation, the C^1, C^{12}, $C^{1'}$, and $C^{12'}$ atoms deviating from the corresponding planes formed by the other atoms of the heteroring (which are coplanar within 0.04 Å) by 0.50, 0.42, 0.44, and 0.50 Å, respectively. The angles between the planes of the phenyl groups and the neighboring 5-membered rings are as follows: C^4–C^9 19.7, C^{15}–C^{20} 10.9, $C^{4'}$–$C^{9'}$ 5.6, and $C^{15'}$–$C^{20'}$ 2.4°, i.e., the "primed" molecule is more planar. The intermolecular contacts are consistent with usual van der Waals interactions.

The formation of bioxazolidine **VII** can be interpreted as a cyclization involving two $HOCHCH_2NHPh$ fragments of molecule **VI** by the action of 2,2-dimethoxypropane (Scheme 5).

Scheme 5.

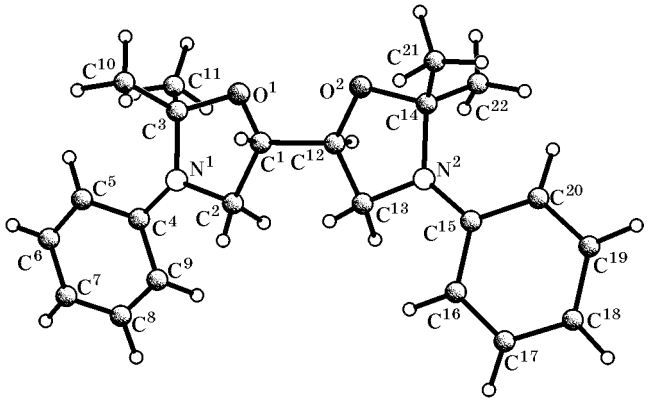


Chiral diamines **Ic** and **VII** were tested as ligands in the catalytic hydrogenation of prochiral substrates, itaconic acid (**VIII**) and α-acetamidocinnamic acid (**IX**), with molecular hydrogen (Table 4). Enantioselective hydrogenation of itaconic acid over rhodium complexes with diamines **Ic** and **VII** yields excess

Table 2. Parameters of intermolecular hydrogen bonds in the crystalline structure of compound **IIIa**

N atom	H atom	O atom	N–H, Å	H···O, Å	N···O, Å	∠NHO, deg	Symmetry transformation
N^1	H^1N^1	O^2	0.90	2.28	3.157	166	$1 - x, 1/2 + y, 3/2 - z$
N^1	H^2N^1	O^3	0.88	2.12	2.906	148	$1 - x, y - 1/2, 3/2 - z$
N^2	H^1N^2	O^4	0.87	2.05	2.907	172	$x - 1/2, 3/2 - y, 1 - z$
N^2	H^2N^2	O^3	0.84	2.01	3.089	155	$x - 1, y, z$

Table. 3. Bond lengths *d* and bond angles ω in the molecule of (5*S*,5′*S*)-2,2,2′,2′-tetramethyl-3,3′-diphenyl-5,5′-bioxazolidine (**VII**)



Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
O^1-C^1	1.420 (3)	$O^{1'}-C^{3'}$	1.417 (3)	C^4-C^5	1.398 (4)	$C^{4'}-C^{9'}$	1.396 (4)
O^1-C^3	1.430 (3)	$O^{1'}-C^{1'}$	1.426 (3)	C^5-C^6	1.382 (4)	$C^{5'}-C^{6'}$	1.371 (4)
O^2-C^{12}	1.417 (3)	$O^{2'}-C^{14'}$	1.424 (3)	C^6-C^7	1.359 (5)	$C^{6'}-C^{7'}$	1.369 (5)
O^2-C^{14}	1.424 (3)	$O^{2'}-C^{12'}$	1.426 (3)	C^7-C^8	1.365 (5)	$C^{7'}-C^{8'}$	1.370 (4)
N^1-C^4	1.381 (3)	$N^{1'}-C^{4'}$	1.385 (3)	C^8-C^9	1.377 (4)	$C^{8'}-C^{9'}$	1.372 (4)
N^1-C^2	1.430 (3)	$N^{1'}-C^{2'}$	1.433 (3)	$C^{13}-C^{13}$	1.512 (3)	$C^{12'}-C^{13'}$	1.506 (3)
N^1-C^3	1.467 (4)	$N^{1'}-C^{3'}$	1.468 (3)	$C^{14}-C^{21}$	1.492 (4)	$C^{14'}-C^{21'}$	1.494 (4)
N^2-C^{15}	1.368 (3)	$N^{2'}-C^{15'}$	1.374 (3)	$C^{14}-C^{22}$	1.507 (4)	$C^{14'}-C^{22'}$	1.508 (4)
N^2-C^{13}	1.426 (3)	$N^{2'}-C^{13'}$	1.436 (3)	$C^{15}-C^{16}$	1.395 (4)	$C^{15'}-C^{20'}$	1.390 (4)
N^2-C^{14}	1.473 (3)	$N^{2'}-C^{14'}$	1.475 (3)	$C^{15}-C^{20}$	1.396 (4)	$C^{15'}-C^{16'}$	1.399 (4)
C^1-C^{12}	1.499 (4)	$C^{1'}-C^{12'}$	1.484 (3)	$C^{16}-C^{17}$	1.376 (4)	$C^{16'}-C^{17'}$	1.378 (4)
C^1-C^2	1.516 (4)	$C^{1'}-C^{2'}$	1.498 (4)	$C^{17}-C^{18}$	1.365 (5)	$C^{17'}-C^{18'}$	1.359 (4)
C^3-C^{11}	1.495 (5)	$C^{3'}-C^{10'}$	1.490 (5)	$C^{18}-C^{19}$	1.365 (4)	$C^{18'}-C^{19'}$	1.374 (4)
C^3-C^{10}	1.505 (5)	$C^{3'}-C^{11'}$	1.510 (5)	$C^{19}-C^{20}$	1.373 (4)	$C^{19'}-C^{20'}$	1.374 (4)
C^4-C^9	1.397 (4)	$C^{4'}-C^{5'}$	1.392 (4)				

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$C^1O^1C^3$	107.7 (2)	$C^{3'}O^{1'}C^{1'}$	110.63 (19)	$C^{11}C^3C^{10}$	112.5 (3)	$C^{10'}C^{3'}C^{11'}$	112.2 (3)
$C^{12}O^2C^{14}$	108.97 (17)	$C^{14'}O^{2'}C^{12'}$	108.72 (18)	$N^1C^4C^9$	120.0 (3)	$N^{1'}C^{4'}C^{5'}$	123.0 (3)
$C^4N^1C^2$	120.6 (2)	$C^{4'}N^{1'}C^{2'}$	121.5 (2)	$N^1C^4C^5$	122.3 (3)	$N^{1'}C^{4'}C^{9'}$	119.8 (2)
$C^4N^1C^3$	126.9 (2)	$C^{4'}N^{1'}C^{3'}$	126.3 (2)	$C^9C^4C^5$	117.7 (3)	$C^{5'}C^{4'}C^{9'}$	117.2 (3)
$C^2N^1C^3$	111.0 (2)	$C^{2'}N^{1'}C^{3'}$	109.8 (2)	$C^6C^5C^4$	120.1 (3)	$C^{6'}C^{5'}C^{4'}$	120.7 (3)
$C^{15}N^2C^{13}$	121.4 (2)	$C^{15'}N^{2'}C^{13'}$	122.3 (2)	$C^7C^6C^5$	121.5 (3)	$C^{7'}C^{6'}C^{5'}$	121.7 (3)
$C^{15}N^2C^{14}$	127.3 (2)	$C^{15'}N^{2'}C^{14'}$	127.0 (2)	$C^6C^7C^8$	119.1 (3)	$C^{6'}C^{7'}C^{8'}$	118.3 (3)
$C^{13}N^2C^{14}$	111.0 (2)	$C^{13'}N^{2'}C^{14'}$	110.67 (19)	$C^7C^8C^9$	121.2 (3)	$C^{7'}C^{8'}C^{9'}$	121.2 (3)
$O^1C^1C^{12}$	110.8 (2)	$O^{1'}C^{1'}C^{12'}$	110.4 (2)	$C^8C^9C^4$	120.5 (3)	$C^{8'}C^{9'}C^{4'}$	120.9 (3)
$O^1C^1C^2$	103.78 (18)	$O^{1'}C^{1'}C2^{'}$	103.8 (2)	$O^2C^{12}C^1$	110.6 (2)	$O^{2'}C^{12'}C^{1'}$	110.1 (2)
$C^{12}C^1C^2$	112.6 (2)	$C^{12'}C^{1'}C^{2'}$	114.7 (2)	$O^2C^{12}C^{13}$	104.68 (18)	$O^{2'}C^{12'}C^{13'}$	103.5 (2)
$N^1C^2C^1$	102.1 (2)	$N^{1'}C^{2'}C^{1'}$	102.3 (2)	$C^1C^{12}C^{13}$	112.1 (2)	$C^{1'}C^{12'}C^{13'}$	114.6 (2)
$O^1C^3N^1$	103.0 (2)	$O^{1'}C^{3'}N^{1'}$	103.7 (2)	$N^2C^{13}C^{12}$	103.2 (2)	$N^{2'}C^{13'}C^{12'}$	102.3 (2)
$O^1C^3C^{11}$	104.9 (3)	$O^{1'}C^{3'}C^{10'}$	107.8 (3)	$O^2C^{14}N^2$	103.3 (2)	$O^{2'}C^{14'}N^{2'}$	102.94 (19)
$N^1C^3C^{11}$	114.8 (3)	$N^{1'}C^{3'}C^{10'}$	112.8 (3)	$O^2C^{14}C^{21}$	104.3 (2)	$O^{2'}C^{14'}C^{21'}$	108.4 (2)
$O^1C^3C^{10}$	109.7 (2)	$O^{1'}C^{3'}C^{11'}$	106.1 (2)	$N^2C^{14}C^{21}$	115.2 (2)	$N^{2'}C^{14'}C^{21'}$	113.0 (2)
$N^1C^3C^{10}$	111.1 (3)	$N^{1'}C^{3'}C^{11'}$	113.6 (3)	$O^2C^{14}C^{22}$	110.3 (2)	$O^{2'}C^{14'}C^{22'}$	105.6 (2)

Table 3. (Contd.)

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$N^2C^{14}C^{22}$	110.8 (2)	$N^{2'}C^{14'}C^{22'}$	113.0 (2)	$C^{17}C^{16}C^{15}$	121.4 (3)	$C^{17'}C^{16'}C^{15'}$	120.8 (3)
$C^{21}C^{14}C^{22}$	112.2 (3)	$C^{21'}C^{14'}C^{22'}$	113.1 (3)	$C^{18}C^{17}C^{16}$	120.6 (3)	$C^{18'}C^{17'}C^{16'}$	121.7 (3)
$N^2C^{15}C^{16}$	120.0 (2)	$N^{2'}C^{15'}C^{20'}$	123.0 (2)	$C^{17}C^{18}C^{19}$	119.1 (3)	$C^{17'}C^{18'}C^{19'}$	118.0 (3)
$N^2C^{15}C^{20}$	123.3 (2)	$N^{2'}C^{15'}C^{16'}$	120.0 (2)	$C^{18}C^{19}C^{20}$	121.2 (3)	$C^{20'}C^{19'}C^{18'}$	121.8 (3)
$C^{16}C^{15}C^{20}$	116.7 (2)	$C^{20'}C^{15'}C^{16'}$	116.9 (2)	$C^{19}C^{20}C^{15}$	121.0 (3)	$C^{19'}C^{20'}C^{15'}$	120.8 (3)

(–)-(*S*)-methylsuccinic acid; however, the optical yield of the product is greater when primary diamine was used as ligand. From α-acetamidocinnamic acid, excess (–)-(*R*)-*N*-acetylphenylalanine was obtained in both cases with moderate optical yields. The low optical yields of the hydrogenation products over rhodium complex with ligand **VII** can be explained by steric factor: because of its large size diamine **VII** is incapable of competing with olefins for coordination site at the transition metal, so that the hydrogenation occurs mainly over achiral rhodium(I) complexes.

EXPERIMENTAL

The NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400 (^{1}H) and 100 MHz (^{13}C) using HMDS as internal reference; the chemical shifts are given relative to TMS. The mass spectra (70 eV) were obtained on an LKB 2091 instrument. GLC analysis was performed on an LKhM-80 chromatograph, equipped with a thermal conductivity detector; 2000 × 3-mm column packed with 5% of SE-30 on Chromaton N-AW-HMDS; carrier gas helium. The optical rotations were measured on a Polamat A spectropolarimeter at λ = 546 nm and were recalculated to λ = 589 with a factor of 1.17543. The X-ray diffraction data were obtained on a Syntex P1 diffractometer (CuK_α irradiation, β-filter, θ/2θ scanning). Arrays of experimental reflections were treated with account taken of the Lorentz and polarization factors, with no regard to X-ray irradiation of the sample. The structures were solved by the direct method and were refined using the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms and isotropic approximation for hydrogen atoms (which were localized experimentally from the difference Fourier syntheses).

Thoroughly purified and degassed solvents were used in the hydrogenation. The catalytic mixtures were prepared under argon using a system which ensured supply of purified gas and the possibility for evacuation. (–)-(*R*,*R*)-DIOP [14] and (*Z*)-α-acetamidocinnamic acid and its methyl ester [15] were prepared by known methods.

(4*S*,5*S*)-4,5-Bis(aminomethyl)-2,2-dimethyl-1,3-dioxolane (Ic). A suspension of 7.72 g (0.2 mol) of $LiAlH_4$ in 170 ml of anhydrous dioxane was refluxed for 30 min, and 14.2 g (0.075 mol) of compound **IIIc** was added in small portions while stirring. When the reaction was complete, the mixture was cooled and filtered, the precipitate was treated with hot dioxane (3 × 150 ml), the extract was combined with the filtrate and evaporated on a rotary evaporator, and the residue was distilled under reduced pressure. Yield 9 g (75%), bp 73–75°C (3 mm), $[\alpha]_D$ = –8.17° (*c* = 8.7, benzene). Mass spectrum, *m*/*z* (I_{rel}, %): 114 (71) $[M - NH_2 - CH_2NH_2]^+$, 72 (100) $[M - CH_2NH_2 - Me_2CO]^+$, 44 (74) $[C_2H_4NH_2]^+$, 30 (54) $[CH_2NH_2]^+$. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 s (6H, Me_2C), 1.55 br.s (2H, NH_2), 2.82 d.m (2H, H_A in CH_2, ^2J = 13.3 Hz), 2.89 d.m (2H, H_B in CH_2, ^2J = 13.3 Hz), 3.77 m (2H, CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.43 (CH_3), 44.32 (CH_2), 80.34 (CH).

(4*R*,5*R*)-2,3-Dihydroxy-*N*,N′-diphenylsuccinamide (IIb). A mixture of 26 g (0.126 mol) of diethyl tartrate, 46 ml (0.5 mol) of aniline, and 20 ml of 1,3,5-trimethylbenzene was heated at 170–175°C with simultaneous distillation of liberated ethanol (for 6–10 h, until 1,3,5-trimethylbenzene began to distil over). After cooling, the colorless crystals were filtered off, washed with chloroform, and dried. Yield 24 g (64%), mp 180°C (decomp.), $[\alpha]_D$ = +87.7° (*c* = 0.35, acetone). Mass spectrum, *m*/*z* (I_{rel}, %): 253 (35) $[M - H_2O - CHO]^+$, 180 (7) $[M - PhNHCO]^+$, 120 (14) $[PhNHCO]^+$, 92 (100) $[PhNH]^+$, 77 (20) $[Ph]^+$. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.50 d (2H, CH, ^3J = 6.5 Hz), 6.02 d (2H, OH, ^3J = 6.5 Hz), 7.07 t (2H, *p*-H, ^3J = 7.4 Hz), 7.31 t (4H, *m*-H, ^3J = 7.9 Hz), 7.74 d (4H, *o*-H, ^3J = 7.2 Hz), 9.59 s (2H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 73.86

(CH), 120.18 (C^o), 124.19 (C^p), 129.25 (C^m), 139.01 (C^i), 171.41 (C=O).

(4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-dicarboxamide (IIIa). A 100-ml high-pressure reactor was charged with 20 g (0.081 mol) of diethyl (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate prepared by cyclization of diethyl tartrate under the action of 2,2-dimethoxypropane. The reactor was cooled to –40°C, 50–70 ml of liquid ammonia was added, and the reactor was closed, kept for 6–8 h at 50°C, cooled to –10°C, opened, and allowed to warm up to room temperature. Excess ammonia was evaporated on a water bath (50–60°C), the released ethanol was removed on heating to 60°C under reduced pressure, and the colorless crystals were dried in a vacuum. Yield 15 g (99%), mp 158–60°C, $[\alpha]_D$ = –12.9° (*c* = 1.66, EtOH). Mass spectrum, *m*/*z* (I_{rel}, %): 173 (16) $[M-CH_3]^+$, 145 (35) $[M-CONH]^+$, 130 (22) $[M-(CH_3)_2CO]^+$, 86 (100) $[130-CONH_2]^+$, 44 (52) $[CONH_2]^+$, 43 (51) $[CONH]^+$. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.39 s (6H, CH_3), 4.43 s (2H, CH), 7.40 s (2H, NH_A), 7.47 s (2H, NH_B). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 26.20 (CH_3), 77.36 (CH), 111.53 (C), 171.34 (C=O). X-Ray diffraction data: $C_7H_{12}N_2O_4$; colorless prism 0.45 × 0.35 × 0.30 mm. Unit cell parameters (rhombic): *a* = 5.3769(6), *b* = 7.7750(9), *c* = 22.092(2) Å; *V* = 923.56(17) Å^3; *Z* = 4, *d* = 1.353 g/cm^3; space group $P2_12_12_1$. Final divergence factors *R* = 0.026, R_w = 0.072 [from 762 reflections with $I > 2\sigma(I)$].

***N*,*N*′-Diphenyloxamide (V).** A mixture of 5 g (0.02 mol) of diethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate and 2.2 g (0.04 mol) of sodium methoxide in 20 ml of aniline was heated at the boiling point in a flask equipped with a high Vigreaux column, a volatile fraction (bp 62–70°C) being distilled off. The boiling point of the mixture rose from 110 to 188°C. The mixture was boiled until volatile products no longer distilled off and was cooled, and the crystals were filtered off, washed with water to neutral reaction, and dried. Yield 4 g (85%), mp 238°C. Mass spectrum, *m*/*z* (I_{rel}, %): 240 (100) M^+, 121 (43) $[M-PhNCO]^+$, 120 (39) $[PhNHCO]^+$, 92 (91) $[PhNH]^+$, 77 (48) $[Ph]^+$. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.16 t (2H, *p*-H, ^3J = 6.7 Hz), 7.38 m (4H, *m*-H), 7.87 d (4H, *o*-H, ^3J = 7.5 Hz), 10.81 s (2H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 120.55 (C^o), 124.73 (C^p), 128.84 (C^m), 137.72 (C^i), 158.70 (C=O). Found, %: C 68.88; H 5.00; N 11.48. $C_{14}H_{12}N_2O_2$. Calculated, %: C 69.99; H 5.03; N 11.66. According to the ^{1}H NMR data and GLC (using authentic samples), the volatile fraction contained methanol, acetone, ethanol, and ethyl acetate.

Table 4. Hydrogenation of itaconic (**VIII**) and α-acetamidocinnamic (**IX**) acids over $[Rh(COD)_2]^+CF_3SO_3^-$ in the presence of diamines **Ic** and **VII** ($c_{Rh} = 2 \times 10^{-3}$ M; MeOH–benzene ratio 2 : 1, diamine–Rh ratio 2 : 1; 25°C)

Ligand	Substrate (S/Rh)	p_{H_2}, atm	Chemical yield, %	Optical yield, % (isomer)
Ic	**VIII**	1	0	–
Ic	**IX**	1	0	–
Ic	**IX** (25)	35	20	2.6 (*R*)
Ic	**VIII** (50)	35	100	25.4 (*S*)
VII	**IX** (25)	35	45	11.1 (*R*)
VII	**VIII** (50)	35	100	7.8 (*S*)

(2*S*,3*S*)-2,3-Dihydroxy-1,4-bis(phenylaminomethyl)butane (VI). Compound **IIb**, 21 g (0.07 mol), was added in small portions while stirring to a suspension of 7 g (0.184 mol) of $LiAlH_4$ in 200 ml of boiling anhydrous dioxane. When the reaction was complete, the mixture was cooled, and the precipitate was filtered off and treated with boiling dioxane (3 × 150 ml). The extract was combined with the filtrate and evaporated on a rotary evaporator, and the residue was recrystallized from chloroform. Yield 11 g (58%), mp 112–115°C, $[\alpha]_D$ = +87.7° (*c* = 0.35, acetone). Mass spectrum, *m*/*z* (I_{rel}, %): 148 (39) $[M-H_2O-PhNHCH_2]^+$, 107 (57) $[PhNHCH_3]^+$, 106 (100) $[PhNHCH_2]^+$, 92 (20) $[PhNH]^+$, 77 (14) $[Ph]^+$. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.99 d.d.d (2H, H_A in CH_2, ^2J = 12.6, ^3J = 7.2, 4.8 Hz), 3.22 d.d.d (2H, H_B in CH_2, ^2J = 12.6, ^3J = 6.7, 4.7 Hz), 3.68 m (2H, CH), 4.68 d (2H, OH, ^3J = 5.9 Hz), 5.35 d.d (2H, NH, ^3J = 4.7, 4.8 Hz), 6.50 t (2H, *p*-H, ^3J = 7.3 Hz), 6.58 d (4H, *o*-H, ^3J = 7.7 Hz), 7.05 t (4H, *m*-H, ^3J = 7.7 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 45.79 (CH_2), 70.04 (CH), 112.11 (C^o), 115.51 (C^p), 128.81 (C^m), 148.99 (C^i). Found, %: C 70.01; H 7.38; N 10.15. $C_{16}H_{20}N_2O_2$. Calculated, %: C 70.56; H 7.40; N 10.29.

(5*S*,5′*S*)-2,2,2′,2′-Tetramethyl-3,3′-diphenyl-5,5′-bioxazolidine (VII). A Soxhlet apparatus was charged with 2 g (7.35 mmol) of compound **VI**, 20 ml of chloroform, 2.5 ml (0.02 mol) of 2,2-dimethoxypropane, 10 mg of *p*-toluenesulfonic acid, and 10 g of 4-Å molecular sieves. The mixture was heated for 7–8 h under reflux and cooled, 20 mg of K_2CO_3 was added, the mixture was filtered and evaporated to dryness, the residue was dissolved in 150 ml of hexane, and the solution was filtered and evaporated to obtain product **VII** as colorless crystals with mp 109–110°C. $[\alpha]_D$ = +35° (*c* = 3.48, benzene).

^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 1.58 s and 1.62 s (6H, CH_3), 3.35 m (1H, H_A in CH_2), 3.47 m (1H, H_B in CH_2), 4.39 m (1H, CH), 6.74 m (6H, *m*-H, *p*-H), 7.18 m (4H, *o*-H); in C_6D_6: 1.42 s (6H, CH_3), 3.03 d.d (1H, H_A in CH_2, ^2J = 8.6, ^3J = 6.1 Hz), 3.13 m (1H, H_B in CH_2), 4.09 m (1H, CH), 6.62 d.d (2H, *m*-H), 6.76 t (1H, *p*-H), 7.14 d.d (2H, *o*-H). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 26.19, 26.28 (CH_3), 49.31 (CH_2), 74.72 (CH), 95.18 (C), 115.17 (C^o), 118.21 (C^p), 129.31 (C^m), 145.02 (C^i). Found, %: C 74.61; H 8.08; N 8.10. $C_{22}H_{28}N_2O_2$. Calculated, %: C 74.97; H 8.01; N 7.95. X-Ray diffraction data: $C_{22}H_{28}N_2O_2$; colorless prism (rhombic), $0.45 \times 0.28 \times 0.25$ mm. Unit cell parameters: a = 10.915(1), b = 17.407(2), c = 20.485(3) Å; V = 3892.1(8) Å^3; Z = 8, d = 1.203 g/cm^3. Space group $P2_12_12_1$. Final divergence factors R = 0.029, R_w = 0.073 [from 2959 reflections with $I > 2\sigma(I)$].

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