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# Note

## Synthesis and resolution of 2,3-diamino-1-cyclohexanols*

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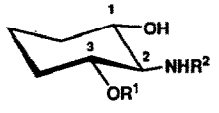
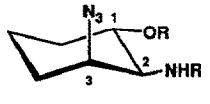
There are four theoretically possible stereoisomers of 2,3-diamino-1-cyclohexanols, each of which is dissymmetric and therefore racemic. The (1,2/3)-[1] and the (1,3/2)-stereoisomer[2] are known, and syntheses of the (1/2,3)- (**6**) and the (1,2,3/0)-stereoisomer (**13**) are now reported.

Starting from known (1,3/2)-2-amino-1,3-cyclohexanediol[3] (**1**), (1/2,3)-2,3-diamino-1-cyclohexanol dihydrochloride (**6**) was prepared as follows. The *N*-(2,4-dinitrophenyl) derivative (**2**) of **1** was heated with 1.2 equiv. of mesyl chloride in pyridine at 0° to give 53% of the monomesylate **3**. Reaction of **3** with sodium azide in *N,N*-dimethylformamide proceeded with inversion of configuration and yielded the azido derivative **4**, after removal of the *N*-(2,4-dinitrophenyl) group. Conventional acetylation of **4** gave the di-*N,O*-acetyl derivative **5**. Catalytic hydrogenation (Pd–C) of **4** in the presence of hydrochloric acid gave the dihydrochloride **6**.

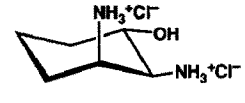
Compound **6** was converted into the di-*N,N'*-acetyl (**7**), 2,3-bis(2,4-dinitropheny-



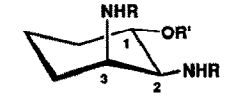

**1** $R^1 = R^2 = H$
**2** $R^1 = H$, $R^2$ = 2,4-dinitrophenyl
**3** $R^1$ = Ms, $R^2$ = 2,4-dinitrophenyl




**4** R = H
**5** R = Ac




**6**




**7** R = Ac, R' = H
**8** R = 2,4-dinitrophenyl, R' = H
**9** R = EtOCO, R' = H
**10** R = R' = Ac

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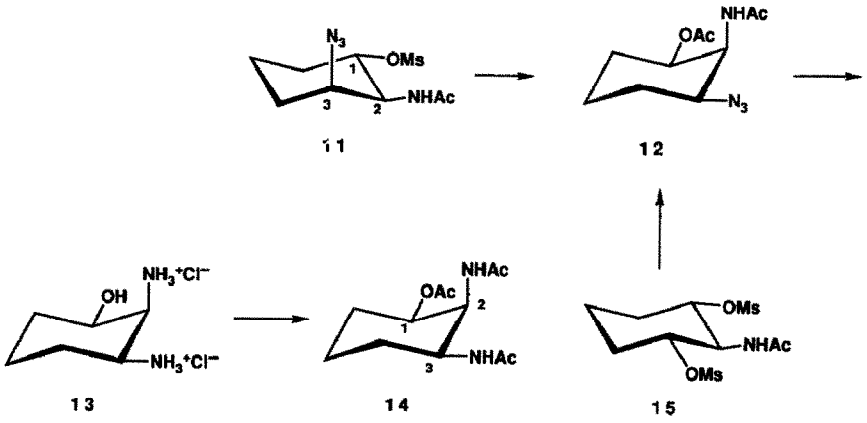
lamino) (**8**), 2,3-bis(ethoxycarbonylamino) (**9**), and tri-*N*,*N*',*O*-acetyl (**10**) derivatives by conventional methods.

The (1/2,3)-isomer **4** was transformed into the desired (1,2,3/0)-isomer **13** by the following reactions. Compound **4** was *N*-acetylated with acetic anhydride in methanol and the product was mesylated to give **11**. Displacement of the mesyloxy group of **11** by acetate ion proceeded with inversion of configuration to give 96% of **12**.

Compound **12** was obtained also as a by-product in low yield (10%) by stepwise replacement of the two mesyloxy groups of known (1,3/2)-2-acetamido-1,3-di-*O*-mesyl-1,3-cyclohexanediol[3] (**15**) with azide ion and then acetate ion. The reaction involved inversions of configurations at C-1 and C-3.

Catalytic hydrogenation (Pd–C) of **12**, followed by hydrolysis with hydrochloric acid, afforded the dihydrochloride **13**, which was converted into the tri-*N*,*N*',*O*-acetyl derivative **14**.




The configurations of **10** and **14** were established by $^1$H-n.m.r. spectroscopy. The spectrum of **10** contained two sharp signals at $\delta$ 2.00 (6 H) and 2.05 (3 H) assigned to equatorial AcO-1 + AcNH-2, and axial AcNH-3, respectively, by an empirical rule[4]. Furthermore, these assignments were coincident with those of **7**. The spectrum of **14** contained three sharp signals at $\delta$ 1.94 (3 H), 2.02 (3 H), and 2.06 (3 H) which were assigned to equatorial AcNH-3, equatorial AcO-1, and axial AcNH-2, respectively.

No enantiomers of the stereoisomeric 2,3-diamino-1-cyclohexanols have been reported hitherto. Optical resolution of the (1/2,3)-isomer **6** was attempted using naproxen [(*S*)-(+)-6-methoxy-α-methyl-2-naphthaleneacetic acid]. Acylation of **6** with naproxen in the presence of triethylamine and 1-[3-(dimethylamino)propyl]-3-ethylcarbodi-imide hydrochloride afforded a mixture of the diastereomeric *N*,*N*',*O*-tris[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-(1/2,3)-2,3-diamino-1-cyclohexanols **16** and **17**, which was fractionated by liquid chromatography. Acid hydrolysis of the diastereomers afforded (−)-(1/2,3)-2,3-diamino-1-cyclohexanol dihydrochloride (**18**), $[\alpha]_D^{22}$ −39°, and the (+)-enantiomer (**19**), $[\alpha]_D^{22}$ +40°. The absolute configurations of **18** and **19** have not yet been established.

## EXPERIMENTAL

*General methods.* — Melting points were determined in capillary tubes and are uncorrected. $^1$H-N.m.r. spectra (internal $Me_4Si$) were recorded with a Varian EM-390 (90 MHz) or XL-300 (300 MHz) spectrometer. I.r. spectra were recorded with a Hitachi HPL-225 spectrometer and optical rotations with a JASCO DIP-140 polarimeter. Column chromatography was performed on Kieselgel 60 (Merck). Preparative medium-pressure liquid chromatography (m.p.l.c.) was performed on a Lobar column (Si60, Merck) with ethyl acetate–hexane. Mass spectra were recorded with a JEOL JMS-HX110 spectrometer. Solutions were concentrated under reduced pressure below 40°.

*(1,3/2)-2-(2,4-Dinitrophenylamino)-1,3-cyclohexanediol* (**2**). — To a stirred solution of (1,3/2)-2-amino-1,3-cyclohexanediol[3] (**1**, 3.0 g) and fluoro-2,4-dinitrobenzene (3.0 g) in methanol (90 mL) was added triethylamine (6.5 mL) dropwise. After 1 h, the solution was concentrated to give **2** (6.2 g, 91%), as reddish orange crystals, m.p. 267–268°.

*Anal.* Calc. for $C_{12}H_{15}N_3O_6$: C, 48.48; H, 5.09; N, 14.14. Found: C, 48.56; H, 4.82; N, 13.97.

*(1,3/2)-2-(2,4-Dinitrophenylamino)-1-O-mesylcyclohexane-1,3-diol* (**3**). — To a stirred solution of **2** (15.0 g) in pyridine (150 mL) was added mesyl chloride (4.7 mL, 1.2 equiv.) under ice cooling. After 1 h, water (10 mL) was added, the mixture was concentrated, and a solution of the residue in ethyl acetate was washed with water, dried ($Na_2SO_4$), and concentrated. The residue was recrystallized from ethyl acetate to give **3** (10.0 g, 53%) as yellow crystals, m.p. 185–186° (dec.). $^1$H-N.m.r. data [$(CD_3)_2SO$]: $\delta$ 1.23–1.97 (m, 6 H), 2.97 (s, 3 H, OMs), 3.50–4.17 (m, 2 H, H-2,3), 4.60–5.07 (m, 1 H, H-1), 5.15–5.20 (bd, 1 H, $J$ 6 Hz, OH), 7.43 (d, 1 H, $J$ 12 Hz, H-5'), 8.23 (dd, 1 H, $J$ 12 and 3 Hz, H-4'), 8.70–8.80 (bd, 1 H, $J$ 9 Hz, NH), 8.88 (d, 1 H, $J$ 3 Hz, H-3').

*Anal.* Calc. for $C_{13}H_{17}N_3O_8S$: C, 41.60, H, 4.57; N, 11.19. Found: C, 41.31; H, 4.52; N, 10.81.

*(1/2,3)-2-Amino-3-azido-1-cyclohexanol* (**4**). — A mixture of **3** (11.1 g) and sodium azide (2.9 g) in *N,N*-dimethylformamide (110 mL) was heated for 2 h at 100° with gentle agitation, then concentrated, and the residue was extracted with ethyl acetate. The extract was washed with water, dried ($Na_2SO_4$), and concentrated. To a solution of the crystalline residue in 2:1 acetone–water (330 mL) was added Amberlite IRA-400 ($HO^-$) resin (220 mL), and the mixture was agitated overnight, filtered, and concentrated. Recrystallization of the residue from ethyl acetate gave **4** (2.4 g, 53%), m.p. 113.5–114°; $\nu_{max}^{KBr}$ 3340 ($NH_2$), 3260 ($NH_2$), 2090 ($N_3$), and 1600 cm$^{-1}$ ($NH_2$).

*Anal.* Calc. for $C_6H_{12}N_4O$: C, 46.14; H, 7.74; N, 35.87. Found: C, 46.07; H, 7.70; N, 35.68.

*(1/2,3)-2-Acetamido-1-O-acetyl-3-azido-1-cyclohexanol* (**5**). — A portion (20 mg) of **4** was treated with acetic anhydride (1 mL) and pyridine (1 mL) overnight. The mixture was concentrated and hexane (2 mL) was added to the residue to give **5** (16 mg, 51%), m.p. 102–103°. $^1$H-N.m.r. data ($CDCl_3$): $\delta$ 1.50–1.77 (m, 6 H), 1.97 (s, 3 H, NHAc), 2.03 (s, 3 H, OAc), 4.01 (ddd, 1 H, $J_{1,2}$ 10, $J_{2,NH}$ 8, $J_{2,3}$ 3 Hz, H-2), 4.13 (bs, 1 H, H-3), 4.97 (bt, 1 H, $J_{1,2}$ 10, $J_{1,6}$ 10, $J_{1,6'}$ 2 Hz, H-1), and 6.20 (bd, 1 H, $J$ 8 Hz, NH).

*Anal.* Calc. for $C_{10}H_{16}N_4O_3$: C, 49.99; H, 6.71; N, 23.32. Found: C, 49.97; H, 6.64; N, 23.56.

*(1/2,3)-2,3-Diamino-1-cyclohexanol dihydrochloride* (**6**). — A portion (1.1 g) of **4** was hydrogenated overnight in the presence of 10% Pd–C (110 mg) in methanol (28 mL) containing conc. hydrochloric acid (2.3 mL) and under a hydrogen pressure of 3.4 kg/cm$^2$. The mixture was filtered and concentrated. Recrystallization of the residue from ethanol gave **6** (1.2 g, 82%), m.p. 213–215°.

*Anal.* Calc. for $C_6H_{14}N_2O{\cdot}2HCl$: C, 35.48; H, 7.94; N, 13.79. Found: C, 35.57; H, 7.61; N, 13.76.

*(1/2,3)-2,3-Diacetamido-1-cyclohexanol* (**7**). — To a solution of **6** (820 mg) in methanol (40 mL) was added 0.5M sodium hydroxide (16 mL). The solution was concentrated, the residue was extracted with ethanol, the extract was concentrated, and the residue was acetylated with acetic anhydride (1.0 mL) in methanol (40 mL) overnight. The solution was concentrated, and the residue was crystallized and recrystallized from ethanol–ether to give **7** (700 mg, 82%), m.p. 164–166°. $^1$H-N.m.r. data (300 MHz, $CDCl_3$ + $CD_3OD$): $\delta$ 1.36–2.10 (m, 6 H), 2.02 (s, 3 H, NHAc), 2.03 (s, 3 H, NHAc), 3.60 (ddd, 1 H, $J_{1,2}$ 9.3, $J_{1,6}$ 4.0, $J_{1,6'}$ 9.2 Hz, H-1), 3.78 (dd, 1 H, $J_{1,2}$ 9.3, $J_{2,3}$ 3.6 Hz, H-2), and 4.32 (ddd, 1 H, $J_{2,3}$ 3.6, $J_{3,4}$ 4.2, $J_{3,4'}$ 4 Hz, H-3).

*Anal.* Calc. for $C_{10}H_{18}N_2O_3$: C, 56.06; H, 8.47; N, 13.07. Found: C, 55.74; H, 8.32; N, 12.80.

*(1/2,3)-2,3-Bis(2,4-dinitrophenylamino)-1-cyclohexanol* (**8**). — A portion (2.0 g) of **6** was converted into the free amine (1.9 g), as described in the preparation of **7**, and a solution in methanol (50 mL) was stirred with fluoro-2,4-dinitrobenzene (4.3 g) and triethylamine (2.5 g), and then stored overnight at 5°. The yellow crystals were collected and recrystallized from methanol to give **8** (3.3 g, 73%), m.p. 137–141°.

*Anal.* Calc. for $C_{18}H_{18}N_6O_9$: C, 46.76; H, 3.92; N, 18.18. Found: C, 46.56; H, 4.12; N, 17.83.

*(1/2,3)-2,3-Bis(ethoxycarbonylamino)-1-cyclohexanol* (**9**). — To a stirred solution of **6** (2.0 g) and sodium hydrogen carbonate (6.7 g) in water (20 mL) was added ethyl chloroformate (3.1 g), and the mixture was stored at ~5° for 2 days. The crystals were collected and washed with cold water and ether to give **9** (2.3 g, 85%), m.p. 118–120°.

*Anal.* Calc. for $C_{12}H_{22}N_2O_5$: C, 52.54; H, 8.08, N, 10.21. Found: C, 52.29; H, 7.97; N, 10.05.

*(1/2,3)-2,3-Diacetamido-1-O-acetyl-1-cyclohexanol* (**10**). — A portion (20 mg) of **6** was treated with acetic anhydride (1 mL) and pyridine (1 mL) overnight. The solution was concentrated and the residue was purified by column chromatography (ethanol–toluene, 1:5) to give **10** (18 mg, 73%), m.p. 183–185°. $^1$H-N.m.r. data ($CDCl_3$): $\delta$ 1.50–1.78 (bs, 6 H), 2.00 (s, 6 H, NHAc and OAc), 2.05 (s, 3 H, NHAc), 4.05–4.28 (m, 1 H, H-2), 4.37–4.57 (m, 1 H, H-3), 4.83–5.07 (bd, 1 H, *J* 8 Hz, H-1), 7.07 (bd, 1 H, *J* 7 Hz, NH), and 7.15 (bd, 1 H, *J* 7 Hz, NH).

*Anal.* Calc. for $C_{12}H_{20}N_2O_4$: C, 56.23; H, 7.87; N, 10.93. Found: C, 56.04; H, 7.80; N, 10.80.

*(1/2,3)-2-Acetamido-3-azido-1-O-mesyl-1-cyclohexanol* (**11**). — A portion (163 mg) of **4** was treated with acetic anhydride (0.15 mL) in methanol (3.0 mL) for 0.5 h. The solution was concentrated, and the residue was treated with mesyl chloride (0.14 mL) and pyridine (3.0 mL). After 2 h, water (0.5 mL) was added, and the mixture was concentrated. The crystalline residue was washed with cold water and dried to give **11** (202 mg, 79%), m.p. 113–114°. $^1$H-N.m.r. data ($CDCl_3$): $\delta$ 1.30–2.35 (m, 6 H), 2.03 (s, 3 H, NHAc), 3.05 (s, 3 H, OMs), 3.90–4.25 (m, 2 H, H-2,3), 4.45–4.80 (m, 1 H, H-1), and 6.53 (bd, 1 H, *J* 9 Hz, NH).

*Anal.* Calc. for $C_9H_{16}N_4O_4S$: C, 39.11; H, 5.84; N, 20.28. Found: C, 39.20; H, 5.77; N, 20.42.

*(1,2,3/0)-2-Acetamido-1-O-acetyl-3-azido-1-cyclohexanol* (**12**). — (*a*) A mixture of **11** (118 mg) and sodium acetate (71 mg) in aqueous 90% 2-methoxyethanol (3.0 mL) was heated for 1 h at 110° with agitation, then concentrated, and the residue was treated with acetic anhydride (2.0 mL) and pyridine (2.0 mL) for 2 h. The solution was concentrated and the residue was recrystallized from ethanol–hexane to give **12** (103 mg, 96%), m.p. 116–120°. $^1$H-N.m.r. data ($CDCl_3$): $\delta$ 1.53–1.90 (m, 6 H), 2.03 (s, 3 H, NHAc), 2.08 (s, 3 H, OAc), 3.70–3.88 (m, 1 H, H-3), 4.38 (dt, 1 H, *J* 9 and 4 Hz, H-2), 4.88–5.07 (m, 1 H, H-1), and 6.20 (bd, 1 H, *J* 9 Hz, NH).

*Anal.* Calc. for $C_{10}H_{16}N_4O_3$: C, 49.99; H, 6.71; N, 23.32. Found: C, 49.81; H, 6.63; N, 23.41.

(*b*) A mixture of (1,3/2)-2-acetamido-1,3-di-*O*-mesyl-1,3-cyclohexanediol[1] (**15**, 2.0 g) and sodium azide (790 mg) in *N,N*-dimethylformamide (20 mL) was heated for 2 h under reflux and then concentrated. The residue was extracted with ethyl acetate, and the extract was washed with water, dried ($Na_2SO_4$), and concentrated. A mixture of the residue and sodium acetate (1.5 g) in aqueous 90% 2-methoxyethanol (10 mL) was heated under reflux for 1 h and then concentrated. The residue was treated with acetic anhydride (8 mL) and pyridine (8 mL) overnight. The crude product was purified by column chromatography (ethanol–toluene, 1:15) to give **12** (150 mg, 10%), m.p. 116–120°, and (1,2/3)-2-acetamido-1-O-acetyl-3-azido-1-cyclohexanol (506 mg, 35%). The latter product was converted into known (1,2/3)-2,3-diacetamido-1-O-acetyl-1-cyclohexanol[2] by catalytic hydrogenation and subsequent acetylation.

*(1,2,3/0)-2,3-Diamino-1-cyclohexanol dihydrochloride* (**13**). — A portion (95 mg) of **12** was hydrogenated in the presence of 10% Pd–C (10 mg) in ethanol (3.0 mL) in a stream of hydrogen. After 3 h, the catalyst was removed, the filtrate was concentrated, the residue was heated in 6M HCl (6 mL) under reflux for 3 h, and the mixture was concentrated. The residue was recrystallized from ethanol to give **13** (40 mg, 50%), m.p. 290–293° (dec.).

*Anal.* Calc. for $C_6H_{12}N_2O{\cdot}2HCl$: C, 35.48; H, 7.94; N, 13.79. Found: C, 35.50, H, 7.64; N, 13.77.

*(1,2,3/0)-2,3-Diacetamido-1-O-acetyl-1-cyclohexanol* (**14**). — A portion (17 mg) of **13** was treated with acetic anhydride (1 mL) and pyridine (1 mL) overnight. The solution was concentrated, and the residue was washed with ether to give **14** (16 mg, 76%), m.p. 207–209°. $^1$H-N.m.r. data ($CDCl_3$): $\delta$ 1.45–1.80 (m, 6 H), 1.94 (s, 3 H,

AcNH-3), 2.02 (s, 3 H, AcO-1), 2.06 (s, 3 H, AcNH-2), 3.75–4.20 (m, 1 H), 4.50–4.75 (m, 1 H), and 4.65–5.00 (m, 1 H).

*Anal.* Calc. for $C_{12}H_{20}N_2O_4$: C, 56.23; H, 7.87; N, 10.93. Found: C, 56.12; H, 7.75; N, 10.95.

*Resolution of (1/2,3)-2,3-diamino-1-cyclohexanol dihydrochloride.* — A mixture of **6** (5.00 g), triethylamine (7.48 g), naproxen (19.8 g), and 4-dimethylaminopyridine (0.30 g) in dichloromethane (300 mL) was agitated until the solution became almost clear. To the stirred solution was added 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (20 g) under ice cooling. After 10 min, the mixture was stirred for 42 h at room temperature, then concentrated, and a solution of the residue in ethyl acetate (200 mL) was washed successively with aqueous 10% citric acid, aqueous 7% sodium hydrogen carbonate, water, and brine, dried ($Na_2SO_4$), and concentrated. M.p.l.c. (ethyl acetate–hexane 2:1 → 3:1 stepwise) of the residue gave, first, *N,N',O*-tris[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-(1/2,3)-2,3-diamino-1-cyclohexanol (**16**; 8.79 g, 47%) and then the more polar diastereomer (**17**; 8.39 g, 44%).

Compound **16**: $^1$H-n.m.r. data (300 MHz, $CDCl_3$): $\delta$ 0.71–0.89 (b, 1 H), 0.94–1.12 (b, 1 H), 1.12–1.6 (bm, 4 H), 1.41 (d, 3 H, *J* 7.2 Hz, CHC*H*$_3$), 1.45 (d, 3 H, *J* 7.2 Hz, CHC*H*$_3$), 1.51 (d, 3 H, *J* 7.2 Hz, CHC*H*$_3$), 3.19 (q, 1 H, *J* 7.2 Hz, C*H*CH$_3$), 3.43 (q, 1 H, *J* 7.2 Hz, C*H*CH$_3$), 3.77 (q, 1 H, *J* 7.2 Hz, C*H*CH$_3$), 3.89 (s, 9 H, 3 MeO), 4.10 (m, 1 H, C*H*NH), 4.23 (m, 1 H, C*H*NH), 4.48 (m, 1 H, C*H*OCO), 5.35 (d, 1 H, *J* 8.7 Hz, NH), 5.41 (d, 1 H, *J* 9.0 Hz, NH), and 7.0–7.8 (m, 18 H). Mass spectrum: *m/z* 767.3740 [(M + H)$^+$; calc. 767.3696].

Compound **17**: $^1$H-n.m.r. data (300 MHz, $CDCl_3$): $\delta$ 0.95–1.60 (bm, 6 H), 1.12 (d, 1.5 H, *J* 7.2 Hz, CHC*H*$_3$), 1.19 (d, 1.5 H, *J* 7.2 Hz, CHC*H*$_3$), 1.26 (d, 1.5 H, *J* 7.2 Hz, CHC*H*$_3$), 1.32 (d, 1.5 H, *J* 7.2 Hz, CHC*H*$_3$), 1.51 (d, 1.5 H, *J* 7.2 Hz, CHC*H*$_3$), 1.56 (d, 1.5 H, *J* 7.2 Hz, CHC*H*$_3$), 2.77 (q, 0.5 H, *J* 7.2 Hz, C*H*CH$_3$), 2.86 (q, 0.5 H, *J* 7.2 Hz, C*H*CH$_3$), 3.32–3.48 (m, 1 H, C*H*CH$_3$), 3.58–3.70 (m, 1 H, C*H*CH$_3$), 3.80–4.04 (m, 10 H, 3 MeO and C*H*NH), 4.26–4.40 (b, 1 H, C*H*NH), 4.48–4.62 (b, 1 H, C*H*OCO), 5.20 (d, 0.5 H, *J* ~9 Hz, NH), 5.23 (d, 0.5 H, *J* ~9 Hz, NH), 5.62 (d, 0.5 H, *J* 8.7 Hz, NH), 5.72 (d, 0.5 H, *J* 8.4 Hz, NH), and 6.8–7.8 (m, 18 H). Mass spectrum: *m/z* 767.3682.

A mixture of **16** (9.10 g) in aqueous 40% ethanol (50 mL) and conc. HCl (60 mL) was heated under reflux for 36 h. Ethanol was evaporated from the mixture, and the residue was washed with ether. The aqueous layer was concentrated and to a solution of the residue (2.42 g) in methanol (30 mL) was added ether (20 mL). The resulting gel-like precipitate was collected and washed with 1:1 methanol–ether and ether to give (−)-(1/2,3)-2,3-diamino-1-cyclohexanol dihydrochloride (**18**; 1.74 g, 72%) as a colorless powder, m.p. 210–212° (dec.), $[\alpha]_D^{22}$ −39° (*c* 1, M hydrochloric acid).

*Anal.* Calc. for $C_6H_{14}N_2O{\cdot}2HCl$: C, 35.48; H, 7.94; N, 13.79. Found: C, 35.26; H, 8.13; N, 13.53.

Analogously, **17** (7.96 g) was converted into the (+)-enantiomer **19** (1.60 g, 76%), isolated as a colorless powder, m.p. 209–211° (dec.), $[\alpha]_D^{22}$ +40° (*c* 1, M hydrochloric acid).

*Anal.* Found: C, 35.25; H, 8.17; N, 13.58.

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