(274–275°): mass spectrum (70 eV) *m/e* 186 (M^+), 169 ($M^+ - 17$), 141 ($M^+ - 45$), 114 ($M^+ - 72$); ir (KBr) 2530 (OH), 1685 cm^{-1} (C=O).

Anal. Calcd for $C_{10}H_6N_2O_2$: C, 64.51; H, 3.23; N, 15.05. Found: C, 64.32; H, 3.25; N, 14.98.

2-Azacycl[3.2.2]azine (Imidazo[2,1,5-*cd*]indolizine, 8). In a 25-ml distillation flask, fitted with a short-path condenser, was placed a mixture of 2-azacycl[3.2.2]azine-4-carboxylic acid (520 mg, 2.79 mmol) and copper powder (600 mg). The flask with its content was cautiously heated with a flame; a reddish liquid was collected on the walls of the flask and the condenser. This liquid was recovered by dissolving it in anhydrous ethyl ether. The liquid was chromatographed over alumina (grade III) and eluted with petroleum ether to give a fluorescing yellow liquid (340 mg, 85.5%), bp 116–118° (0.2 Torr), which darkens eventually: ^1H NMR, see Table I; mass spectrum (70 eV) *m/e* 142 (M^+), 115 ($M^+ - 27$).

Anal. Calcd for $C_9H_6N_2$: C, 76.05; H, 4.22; N, 19.73. Found: C, 74.91; H, 4.58; N, 19.24.

Preparation of Compound 12.[8] To a stirred solution of 4-formyl-2-azacycl[3.2.2]azine (0.102 g, 0.72 mmol) in 20 ml of pure acetone was added a basic solution of Ag_2O (prepared from 270 mg of $AgNO_3$ in 4 ml of water and 127 mg of NaOH in 4 ml of water). The mixture was stirred at room temperature for 1.5 hr, and the filtrate was concentrated under reduced pressure. Acidification with 5% HCl to pH 5 and evaporation of the solution to dryness gave a dark red solid, which was further purified by sublimation to afford a fluorescing red-brick solid (110 mg, 88%): mp 159–161°; ^1H NMR, see Table I; mass spectrum (70 eV) *m/e* 210 (M^+), 195 ($M^+ - 15$), 167 ($M^+ - 43$), 140 ($M^+ - 70$); ir (Nujol) 1650 [M^{-1} (>C=O)], 1605 cm^{-1} (>C=C<), enhanced absorption.

Anal. Calcd for $C_{13}H_{10}N_2O$:C, 74.29; H, 4.76; N, 13.33. Found: C, 74.15; H, 4.80; N, 13.37.

Preparation of Compound 11.[7] To a stirred solution of 20.7 ml of 2 *M* BuLi (in hexane) and 20 ml of anhydrous ethyl ether was added imidazo[1,5-*a*]pyridine (1.085 g, 8.22 mmol) in 20 ml of THF and under a N_2 atmosphere at 0°. Then DMF (2.4 g, 32.9 mmol) in ether was added at once and the mixture was stirred for an additional 15 min. The reaction mixture was treated with 10 ml of water, acidified with 5% HCl, and washed with ethyl ether. The aqueous layer was made basic with anhydrous Na_2CO_3 and extracted with chloroform. Evaporation of the solvent under reduced pressure gave a dark solid which was chromatographed (neutral Al_2O_3 grade III) and eluted with a 27:75 mixture of hexane–benzene. The second fraction afforded a highly fluorescing reddish solid (55 mg, 3.5%): mp 162–163°; ^1H NMR, see Table I; mass spectrum (70 eV) *m/e* 238 (M^+), 239 ($M^+ - 1$), 209 ($M^+ - 29$), 181 ($M^+ - 57$), 155 ($M^+ - 83$), 142 ($M^+ - 96$); ir (Nujol) 1655 (>C=O), 1605 cm^{-1} (>C=C<).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.88; N, 11.75. Found: C, 75.56; H, 6.11; N, 11.47.

Registry No.—**1**, 209-81-4; **2**, 10558-77-7; **3**, 1122-72-1; **3** oxime, 1195-40-0; **4**, 54384-88-2; **5**, 6558-64-1; **6**, 54446-41-2; **7**, 54384-89-3; **8**, 54384-90-6; **11**, 54384-91-7; **12**, 54384-92-8; hydroxylamine hydrochloride, 5470-11-1; 6-methyl-2-aminomethylpyridine, 6627-60-7.

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(7) Compound **11** was obtained during the course of our investigation on the reaction of 5-methylimidazo[1,5-*a*]pyridine with BuLi and DMF. It was found that by using a 1:5:1 ratio of the reactants the main product was compound **11**. No attempt was made to improve the yield.
(8) Compound **12** was obtained during one attempt to oxidize the 4-formyl derivative (**6**) with basic silver oxide when acetone was used as solvent.

Hydrazinolysis of 1-Phenylethane Diazotate. A New Synthesis of 1-Phenylethylhydrazine (Mebanazine)[1]

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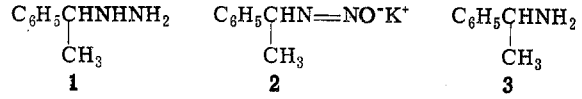
Conversion of 1-phenylethylamine to 1-phenylethane diazotate, followed by treatment of the diazotate with hydrazinium sulfate in anhydrous hydrazine, afforded 40% 1-phenylethylhydrazine (isolated as the oxalate), 35% styrene, and 15% 1-phenylethanol. Starting with optically active 1-phenylethylamine, optically active 1-phenylethylhydrazine was obtained with 54% net inversion of configuration and optically active 1-phenylethanol was obtained with 66% net retention of configuration. In peripheral experiments, optically active 1-phenylethylhydrazine and 1-phenylethylamine were catalytically reduced to optically active 1-cyclohexylethylamine.

Although the synthesis of monoalkylhydrazines is problematical,[3] a number of practical methods exist. These include the direct alkylation of hydrazine or hydrazine hydrate,[4] reaction of azines with Grignard reagents,[5] conversion of alkylamines to sydnones and thence to alkylhydrazines,[6] amination of alkylamines with chloramine[7] or hydroxylamine-*O*-sulfonic acid,[8] and syntheses of *N*-alkyldiaziridines (which may be cleaved to monoalkylhydrazines).[9,10]

For another project, we required substantial quantities of (optically active) 1-phenylethylhydrazine (**1**).[11] *Racemic*



1 **2** **3**

1 has been prepared from *N*-1-phenylethyl-*N,N'*-dicarboethoxyhydrazine,[12] and also by the direct alkylation of hydrazine or its hydrate with 1-phenylethyl halides,[13] by the catalytic reduction of acetophenone azine,[14] and by reaction of acetaldehyde azine with phenylmagnesium bromide, followed by hydrolysis of the resulting acetaldehyde 1-phenylethylhydrazone.[5] However, the only reported preparation of optically active **1** appears to be that of Kopecky and Gillan, who prepared (*S*)-(−)-**1** from (*S*)-(−)-1-phenylethylamine in 8% yield via amination with hydroxylamine-*O*-sulfonic acid.[15]

The poor yield afforded by this procedure led us to develop an alternative synthesis. Because ammonolysis of optically active 1-phenylethane diazotate (**2**) affords 1-phenylethylamine (**3**) with 46% net inversion,[16] we anticipated

that hydrazinolysis of **2**, derived[17] from optically active **3**, would afford the desired hydrazine, **1**, in reasonable yield and with substantial optical activity. We report here the successful outcome of this sequence, and comment briefly on mechanistic aspects of the results.

1-Phenylethylamine (**3**) was converted to the corresponding urethane and nitrosated with N_2O_4–ether, and the resulting *N*-nitroso-*N*-1-phenylethylurethane was cleaved[17] to diazotate **2** with KO-*t*-Bu in ether. A hydrazine solution of **2** was treated with 2 equiv of hydrazinium sulfate in hydrazine at 0–5°. The addition required 2 hr, during which 95% of the theoretical nitrogen content of **2** was evolved.

From the reaction mixture, we isolated 40% of the desired 1-phenylethylhydrazine (**1**) as its oxalate salt; 35% styrene and 15% 1-phenylethanol were also present. Product identities were established by comparison with authentic samples.

Two repetitions of this experiment with **2** derived from (*R*)-(+)-**3**, $\alpha^{22}D$ + 3.638° (neat, 0.1 dm),[18a] 95.0% optically pure,[18b] each gave optically active **1** and 1-phenylethanol. The alcohol samples, purified by GC, had $\alpha^{25}D$ + 2.743° and $\alpha^{25}D$ + 2.747°, each corresponding to an optical purity of 62.7%.[19] The stereochemical course of the (*R*)-**2** → (*R*)-(+)-1-phenylethanol conversion was therefore 66.0% *net retention*.[20]

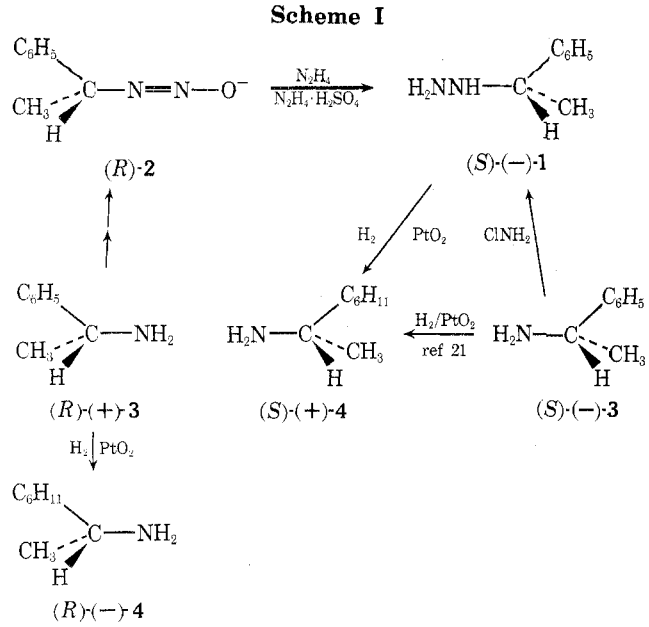
The stereochemistry of the (*R*)-**2** → **1** transformation was determined by three methods.

(1) Two hydrazinolyses of (*R*)-**2** gave samples of optically active **1** which were completely converted to the oxalate salts. Hydrogenation of the salts over PtO_2 afforded two samples of 1-cyclohexylethylamine (**4**), which, after GC purification, had $\alpha^{25}D$ +0.150° and $\alpha^{25}D$ +0.154° ($\alpha^{15}D$ +0.170°).

Leithe[21] reported $[\alpha]^{15}D$ +3.2°, $\alpha^{15}D$ +2.8° (neat, 1 dm) for optically pure (*S*)-(+)-**4** prepared by catalytic reduction of (*S*)-(−)-**3**. In our hands, reduction of 95% optically pure (*R*)-(+)-1-phenylethylamine gave (*R*)-(−)-1-cyclohexylethylamine, $\alpha^{15}D$ −0.317°. This affords an apparent value of $\alpha^{15}D$ −3.34° (neat, 1 dm) for optically pure **4**.

Using the latter value, and the observation (above) that 95% optically pure (*R*)-**2** gave, via hydrazinolysis followed by reduction, (*S*)-(+)-**4**, $\alpha^{15}D$ +1.70° (neat, 1 dm), the stereochemical course of the **2** → **1** conversion must have been 53.6% *net inversion*. The stereochemical relationships are summarized in Scheme I.

Scheme I



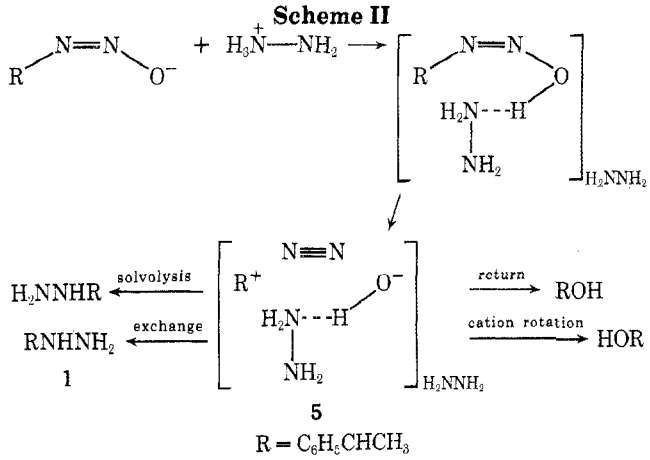
(2) Despite Leithe's report,[21] we were concerned about the possibility of racemization during the catalytic reduction of **1** or **3** to **4**.[22] Therefore, authentic (*S*)-(−)-**1** was prepared from (*S*)-(−)-**3** using the chloramine method.[7] From (*S*)-(−)-**3**, $\alpha^{22}D$ −3.636°, 95% optically pure,[18b] we obtained 10% of **1** oxalate. Without recrystallization, this material had $[\alpha]_{365}^{31.5}$ −10.5° (*c* 0.40, water).[23a] From hydrazinolysis of 95% optically pure (*R*)-**2**, we obtained a sample of **1** oxalate which had $[\alpha]_{365}^{31.5}$ −5.8° (*c* 0.60, water).[23b] Assuming that the former value represents optically pure **1** oxalate, comparison of the two experiments gives 5.8/10.5 = 55% *net inversion* for the **2** → **1** hydrazinolysis, which compares well with the 53.6% net inversion determined by method 1.

(3) Finally, the (*S*)-(−)-**1** formed by hydrazinolysis of 95% optically pure (*R*)-**2** was purified by GC on a Penwalt column at 160°. This sample of hydrazine **1** had $[\alpha]^{25}D$ −16.57° (*c* 2.902, benzene).[24] Comparison with $[\alpha]^{25}D$ −30.3° (*c* 0.784, benzene), which may be calculated for optically pure (*S*)-(−)-**1**,[25] determines the stereochemical course of the **2** → **1** hydrazinolysis as 54.7% *net inversion*, which agrees very well with the previous determinations.

Hydrazinolysis of optically active 1-phenylethane diazotate does indeed give 1-phenylethylhydrazine in reasonable yield and with substantial optical activity. Because the diazotate is easily obtained from 1-phenylethylamine,[17] the entire sequence constitutes a useful preparative method.

The formation of inverted **1** and retained 1-phenylethanol in the hydrazinolysis of **2** is mechanistically analyzed in Scheme II.

Scheme II



R = $C_6H_5CHCH_3$

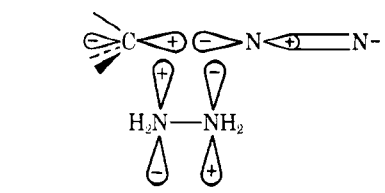
1 arises mainly by inverting hydrazinolysis of nitrogen-separated ion pair **5**, although front-side participation of hydrazine (hydrogen bonded to the hydroxide counterion) competitively affords retained **1** ("exchange" pathway), and precludes complete solvolytic inversion. The retained 1-phenylethyl alcohol forms largely by hydroxide return within **5**. Failure to obtain complete retention suggests the occurrence of cation rotation–collapse.[26]

Analogous diazotate solvolyses have been discussed in detail.[27] Here, we wish only to compare the hydrazinolysis stereochemical results with those obtained in the *ammonolysis* of **2**.[16] The *overall* stereochemistry of the return process (**2** → 1-phenylethanol) is 80% retention in ammonolysis,[16] and 83% retention in hydrazinolysis. The similar values support our conclusion that the extent of retention in deaminative return reactions depends mainly on *cation identity*, and less strongly on the nature of the solvent or the counterion.[27a]

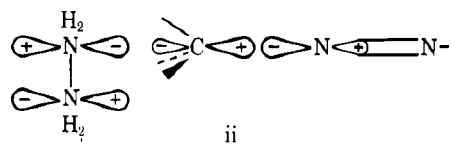
The *overall* stereochemistry of the solvolysis pathways (**2** → **3** or **2** → **1**) is 73% inversion in ammonolysis[16] and

77% inversion in hydrazinolysis. Little increase in inversion is noted when ammonia is replaced by the more nucleophilic hydrazine. Nor is there any stereochemical abnormality attributable to an "α effect" in the latter case.[28] This is perhaps not surprising, because the effect is not believed to operate at tetrahedral carbon,[29] and because hydrazine is probably present at front *and* rear sides of both 5 and its covalent precursor; see Scheme II.

However, one could have speculated a priori that an α nucleophile could preferentially react from the front side at tetrahedral carbon, i.e., with *retention*. Such an arrangement, i, might allow energetically favorable overlap of the (antisymmetric) HOMO of hydrazine and the σ^* (LUMO) of the substrate C–N bond, which could be preferable to (inverting) back-side attack, ii.[30,31] It is clear, however, that this possibility is not realized in the hydrazinolysis of 1-phenylethane diazotate, which proceeds with high inversion.[32]



i



ii

Experimental Section

1-Phenylethylurethane. 1-Phenylethylamine, distilled from Na (bp 59–60°, 6 Torr), was converted to 1-phenylethylurethane by treatment with ethyl chloroformate and K_2CO_3 in water and benzene, according to the method of Bortnick.[33] From 35 g of amine, we obtained 50 g (89%) of the urethane: bp 93–95° (0.25 Torr) [lit. bp 173° (23 Torr)];[34] infrared (film) 1715 cm^{-1} (C=O); NMR[35] (CCl_4) δ 7.20 (m, 5 H, phenyl), 5.67 (broad, 1 H, NH), 4.76 (quintet, J = 7 Hz, 1 H, benzylic), 4.00 (q, J = 7 Hz, 2 H, OCH_2), 1.38 (d, J = 7 Hz, 3 H, $CHCH_3$), and 1.12 (t, J = 7 Hz, 3 H, CH_2CH_3).

(+)-1-Phenylethylurethane ($\alpha^{24.5}D$ +8.487°)[18a] was similarly derived from Aldrich (+)-1-phenylethylamine ($\alpha^{22}D$ +3.638°, 95.0% optically pure,[18b] distilled from Na).

1-Phenylethane Diazotate (2). The 1-phenylethylurethane was nitrosated with N_2O_4 in ether, as described by Moss.[17] The NMR of the crude *N*-1-phenylethyl-*N*-nitrosourethane (CCl_4) showed, inter alia, δ 5.98 (q, J = 7 Hz, 1 H, benzylic) and 4.35 (q, J = 7 Hz, 2 H, OCH_2). The deshielding of these protons ($\Delta\delta$ = 1.22 and 0.35, respectively) is characteristic for the urethane → *N*-nitrosourethane conversion.[36]

The diazotate 2 was prepared by treating 5.0 g (22 mmol) of the nitrosourethane with 5.0 g (43 mmol) of potassium *tert*-butoxide in anhydrous ether at −30°, according to the general procedure of Moss.[17]

1-Phenylethylhydrazine (1). Ether was stripped from the solid diazotate 2, and 25 ml of anhydrous hydrazine[37] was added. The resulting hydrazine solution of 2 was cooled to 0–5° and stirred magnetically, while a solution of 5.59 g (43 mmol) of hydrazinium sulfate in 25 ml of anhydrous hydrazine was slowly added from an addition funnel. Nitrogen evolution occurred during the addition and amounted to 468 ml (95%).

After the addition step was completed, the reaction mixture was stirred at 25° for 10 hr. Hydrazine was distilled away under reduced pressure in a nitrogen atmosphere (20 Torr). The residue was extracted with 3 × 25 ml of ether; the ether was stripped, and the residual crude 1 was distilled to afford 1.21 g (8.9 mmol, 40%) of pure 1-phenylethylhydrazine, bp 83° (1.3 Torr) [lit.[5] bp 75° (1.1 Torr)].

A solution of 1.1 g (8.8 mmol) of oxalic acid in 8 ml of absolute ethanol was added to the product 1. The resulting white, solid 1 oxalate was filtered, washed with ether, and dried,[38] mp 169–170° (lit.[5] mp 170–171°).

The NMR spectrum of 1 (CCl_4) showed δ 7.23 ("s", 5 H, phenyl), 3.63 (q, J = 7 Hz, 1 H, benzylic), 2.97 (broad s, 3 H, NH), and 1.25 (d, J = 7 Hz, 3 H, CH_3).

Authentic 1 and 1 oxalate were prepared by "method B" of Overberger and DiGiulio;[5] the 1 oxalate had mp 169–170°. Both compounds were identical with the corresponding hydrazinolysis products (melting point or NMR).

Authentic 1 and 1 oxalate were also prepared from 1-phenylethylamine and chloramine, according to the procedure of Audrieth.[7] The 1 oxalate thus obtained had mp 169–170°. All 1 oxalate samples were dried at 78° (1 Torr) for 12 hr.

Anal. Calcd for $C_{10}H_{14}O_4N_2$ (oxalate): C, 53.09; H, 6.23; N, 12.38. Found: C, 52.83; H, 6.24; N, 12.32 (by the synthesis of ref 5); C, 52.87; H, 6.18; N, 12.34 (by the procedure of ref 7).[39]

Repetition of the hydrazinolysis experiment with 95.0% optically pure diazotate 2 afforded optically active 1 and 1 oxalate. Rotations and optical purities are discussed in the text.

Other Hydrazinolysis Products. Hydrazinolysis of 2, as above, afforded a reaction mixture which was diluted with 50 ml of water. The mixture was extracted with 3 × 20 ml of ether. The combined ethereal extract was washed with 25 ml of 6 *N* HCl and with distilled water (3 × 50 ml). The ethereal solution was dried ($MgSO_4$) and stripped at 0° to afford a residue which contained styrene and 1-phenylethanol (GC on a 12 ft × 0.25 in., 5% Carbowax 20M on 90/100 ABS column at 160°). Absolute yields (styrene, 35%; 1-phenylethanol, 15%) were determined by GC, relative to a dodecane internal standard. 1-Phenylethanol did not dehydrate under these conditions. From 95.0% optically pure 2, optically active 1-phenylethanol was obtained (see text).

Reduction of 1. 1-Phenylethylhydrazine oxalate (2.0 g, 6 mmol), in 50 ml of water, and 0.2 g of PtO_2 were contained in pressure vessel and attached to a Paar hydrogenation apparatus. After 48 hr, under 46 psig of hydrogen, the reaction solution was filtered, brought to pH >12 with NaOH pellets, and extracted with 4 × 25 ml of ether. The ethereal extract was dried (BaO) and stripped at 0°. Purification of the residual oil on a 10 ft × 0.25 in., 28% Penwalt 223, 4% KOH on 80/100 Gas Chrom R column at 178° gave 1-cyclohexylethylamine (4). The NMR spectrum (CCl_4) showed δ 2.61 (m, 1 H, H_2NCH), 1.71 and 1.06 (m, cyclohexyl and NH_2), and 1.00 (d, J = 7 Hz, CH_3). The remainder of the protons had an integral weight of 16, relative to the δ 2.61 proton.

Optically active 1-phenylethylamine (3) was similarly reduced to 4, and purified on the Penwalt column. Rotational and optical purity data for this reduction and for the reduction of optically active 1 oxalate are described in the text.

Control Experiments. Styrene (5.0 g, 4.8 mmol) was stirred with 10 ml of hydrazine and 1 g of hydrazine sulfate for 14 hr at 25°. The resulting mixture was diluted with 100 ml of 10% aqueous NaOH solution and the whole was extracted with 3 × 30 ml of ether. The ethereal extract was dried (Na_2CO_3) and stripped to afford a residue which was examined by GC on the Penwalt column (see above) at 170°. No 1-phenylethylhydrazine was detected. Under comparable GC and concentration conditions, 1% of 1-phenylethylhydrazine could be detected. Hence, under our hydrazinolysis conditions, N_2H_4 does not add to product styrene to give (racemic) 1.

(+)-1-Phenylethanol, $\alpha^{27}D$ +0.648°[18a] (1.0 g, 8.1 mmol), was stirred overnight with 10 ml of hydrazine and 1 g of hydrazine sulfate. The reaction solution was extracted with 3 × 25 ml of ether. The ether extract was washed with water and added to 3 g of oxalic acid in 15 ml of ethanol. The white precipitate was filtered and examined by NMR. It did not contain 1 oxalate. The filtrate was stripped and the residue was purified by GC on the Carbowax column to afford 1-phenylethanol of unchanged optical activity, $\alpha^{27}D$ +0.650°.

Acknowledgments. We thank the National Institutes of Health (CA 14912) and the National Science Foundation (GP 32159X) for financial support. We also thank Professor N. Epiotis for helpful discussions.

Registry No.—1, 54422-98-9; (*S*)-(−)-1, 24292-42-0; 1 oxalate, 54422-99-0; (*S*)-(−)-1 oxalate, 54384-30-4; 2, 54423-00-6; (*R*)-2, 29882-69-7; 3, 300-62-9; (*R*)-(+)-3, 3886-69-9; (*S*)-(−)-3, 2627-86-3; 4, 54423-01-7; (*R*)-(−)-4, 5913-13-3; (*S*)-(+)-4, 17430-98-7; 1-phenylethylurethane, 54423-02-8; ethyl chloroformate, 541-41-3; (+)-1-phenylethylurethane, 14185-43-4; *N*-1-phenylethyl-*N*-nitrosourethane, 54744-26-4; 1-phenylethanol, 13323-81-4; (*R*)-1-phenylethanol, 1517-69-7; oxalic acid, 144-62-7.

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(23) (a) $\alpha^{31.5}_{365}$ −0.040° (1 dm). The specific rotation given in the text is corrected for the optical purity of the amine precursor. (b) $\alpha^{31.5}D$ −0.033° (1 dm). The specific rotation is corrected for the optical purity of the amine.
(24) $\alpha^{25}D$ −0.457° (*c* 2.902, benzene, 1 dm). The specific rotation is corrected for the optical purity of the diazotate precursor.
(25) Reaction of 95.6% optically pure (*S*)-(−)-**3** with hydroxylamine-*O*-sulfonic acid gave 8% of pure (*S*)-**1**, $[\alpha]^{25}D$ −29.0° (*c* 0.784, benzene).[15]
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Synthesis of Phenyl-Substituted 1-Aminotetralines

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Synthetic methods were developed for 1-, 2-, 3-, or 4-phenyl-substituted 1-aminotetraline derivatives. 1-Phenyl-1-aminotetraline was obtained by hydrazoic acid addition to 1-phenyl-3,4-dihydronaphthalene, followed by lithium aluminum hydride reduction. The cis isomers of 2- or 3-phenyl-substituted *N*-methyl-1-aminotetraline resulted from sodium borohydride reduction of the methylimines derived from the corresponding ketones. Sodium borohydride treatment of the methylimine derived from 4-phenyl-1-tetralone gave a 1:1 mixture of *cis*- and *trans*-4-phenyl-1-aminotetraline, but stereoselective conversions were achieved by catalytic hydrogenation over palladium/carbon (cis isomer) and by zinc–acetic acid reduction (trans isomer). These reactions were extended to the synthesis of the corresponding 5-methoxy-8-chloro substituted analogs and to the preparation of a series of 4-phenyl-1-aminotetralines with modified nitrogen substituents. In addition, two useful reactions were discovered: the oxidation of 1-phenyltetraline to 4-phenyl-1-tetralone with potassium permanganate and the conversion of *N*-methyl-4-phenyl-1-aminotetraline to the corresponding ketone by aqueous potassium permanganate.

The interesting pharmacological activity exhibited by certain 1-aminotetralines,[1] especially the 5-methoxy-8-halogen derivatives, prompted us to investigate the synthesis of 1-aminotetralines substituted with phenyl groups in the alicyclic ring. Initially, we explored the synthesis of the simple 1-, 2-, 3-, or 4-phenyl-substituted 1-aminotetralines bearing no substituents in the aromatic ring. The synthesis of 1-phenyl-1-aminotetraline was approached in three ways. Addition of phenylmagnesium bromide or phenyllithium to the methylimine (**1**) derived from 1-tetralone (**4**) failed to give, even in the presence of polarizing agents such as BF_3, the desired 1-phenyl-1-aminotetraline derivative **2** (Scheme I), although this type of reaction had been successful in the preparation of the corresponding 1-methyl derivatives.[1] While this failure may be due to steric factors, this explanation is not entirely satisfactory, since the reaction of phenylmagnesium bromide with 1-tetralone (**4**) itself proceeded in good yield in accordance with published results[2,3] to the alcohol **5**. Compound **5** was dehydrated to 3,4-dihydro-1-phenyltetraline (**6**),[2] which proved to be inert in the Ritter reaction[4] (acetonitrile, sulfuric acid). The modified conditions of Chow et al.[5] (acetonitrile, mercuric nitrate) led, presumably via **7**, to the mercurated olefin **10**. The addition of hydrazoic acid to **6** in the presence