Quinoxaline Studies. XVI.[1a] Unequivocal Synthesis of (S)-2-Methyl-1,2,3,4-tetrahydroquinoxaline

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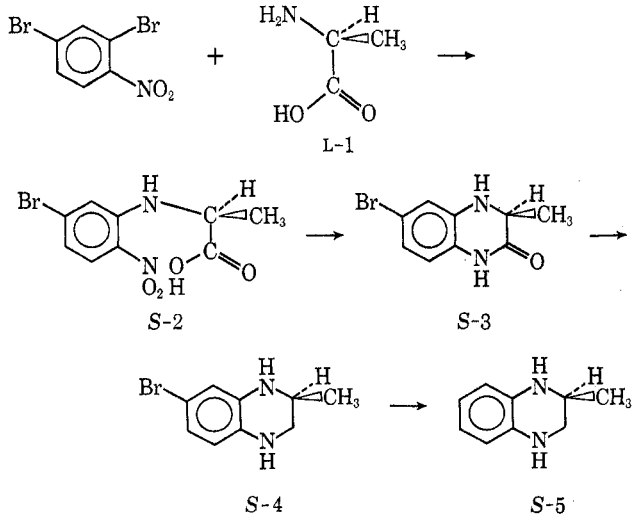
The unequivocal synthesis of (*S*)-2-methyl-1,2,3,4-tetrahydroquinoxaline *via* the sequence L-α-alanine (L-**1**), (*S*)-N-(2-nitro-5-bromophenyl)-α-alanine (*S*-**2**), (*S*)-3-methyl-6-bromo-3,4-dihydro-2(1H)-quinoxalinone (*S*-**3**), (*S*)-2-methyl-7-bromo-1,2,3,4-tetrahydroquinoxaline (*S*-**4**), and (*S*)-2-methyl-1,2,3,4-tetrahydroquinoxaline (*S*-**5**) is described, as well as the resolution of *RS*-**5** into *R*-**5**. Physical properties and derivatives are reported for the above compounds.

The 2-quinoxaloyl unit present in triostin and quinomycin antibiotics[2] has not as yet had its biological source elucidated. The authors conjecture that the 2-quinoxalinecarbonyl unit may form *in vivo* initially in the reduced state *via* condensation of 2,3-diaminopropanoic acid with catechol to give 1,2,3,4-tetrahydro-2-quinoxalinecarboxylic acid, or with 5-dehydroshikimic acid to give 2-decahydroquinoxalinecarboxylic acid. Tetrahydroquinoxalines are also of interest as models for tetrahydrofolic acid.[3]

The purpose of this paper is to report the unequivocal synthesis of (*S*)-2-methyl-1,2,3,4-tetrahydroquinoxaline (*S*-**5**) as a potential configurational standard for all future work dealing with 2-substituted reduced quinoxalines. Because of ready availability, L-α-alanine was utilized to provide the asymmetric center of **5**.

The synthesis of **5** was executed *via* the sequence L-α-alanine (L-**1**), (*S*)-N-(2-nitro-5-bromophenyl)-α-alanine (*S*-**2**), (*S*)-3-methyl-6-bromo-3,4-dihydro-2(1H)-quinoxalinone (*S*-**3**), (*S*)-2-methyl-7-bromo-1,2,3,4-tetrahydroquinoxaline (*S*-**4**), and finally (*S*)-2-methyl-1,2,3,4-tetrahydroquinoxaline (*S*-**5**) (Scheme I).

SCHEME I



Initial work commenced with DL-α-alanine, and after chemical problems related to the preparation of the above series had been solved, the work was repeated using optically active α-alanine. No marked differences between the racemic and the optically active compounds were observed. As expected, *RS*-**2**, *RS*-**3**, and *RS*-**5** were lower melting than *S*-**2**, *S*-**3**, and *S*-**5**; however, *RS*-**4** was higher melting than *S*-**4**.

The Br atom of *o*-bromonitrobenzene was not displaced by the nucleophilic amine nitrogen attack of α-alanine. Hence, increased activity of the Br was sought by having a second negative group appropriately disposed on the benzene ring. Although the carboxyl,[4,5] the carbomethoxy,[6] and the nitro[7,8] groups have been utilized for just such activation roles, the replacement of these groups with H requires too lengthy a synthetic sequence. Therefore, 2,4-dibromonitrobenzene was chosen as the portal compound for the above series, because the *p*-Br was expected, by a one-step hydrogenolysis reaction, to subsequently yield its place (in **4**) to H.

N-(2-Nitro-5-bromophenyl)-α-alanine (**2**) was prepared by condensing α-alanine (**1**) with 2,4-dibromonitrobenzene by a modification of the method of Van Dusen and Schultz.[9] Inverse addition of the reagents (aqueous $KHCO_3$–alanine to alcoholic 2,4-dibromonitrobenzene) was found effective in preserving homogeneity of the reaction solution and affording good yields of **2**.

Stannous chloride reduction of **2** to **3** gave consistently good yields. However, catalytic reduction displayed the following surprising results. Raney nickel catalyst reduction of the K salt of **2** in H_2O afforded moderate yields of **3**. Palladium–charcoal catalyst gave infuriatingly nonreproducible results: generally (but not always) in aprotic THF good yields of **3** were obtained, whereas in protic EtOH tars and/or hydrogenolysis of Br were observed, yielding 3-methyl-2(1H)-quinoxalinone (*via* 3-methyl-3,4-dihydro-2(1H)-quinoxalinone, which spontaneously dehydrogenated during isolation).

The Br of **3** played the fortuitous role of stabilizing **3**; however, **3** dehydrogenated to 3-methyl-6-bromo-2(1H)-quinoxalinone[9] with heating, prolonged standing in organic solvents, or passage through an alumina

(1) (a) Part XV: H. R. Moreno and H. P. Schultz, *J. Med. Chem.*, **13**, 119 (1970); (b) NSF Trainee, 1969–present; (c) NSF Trainee, 1966–1967; abstracted in part from the M. S. thesis of P. J. W.

(2) H. Otsuka and J. Shoji, *Tetrahedron*, **23**, 1535 (1967), and references therein.

(3) S. J. Benkovic, P. A. Benkovic, and D. R. Comfort, *J. Amer. Chem. Soc.*, **91**, 5270 (1969).

(4) F. Micheel, K. Weichbrodt, and J. Plenikowski, *Justus Liebigs Ann. Chem.*, **581**, 242 (1953).

(5) W. Blackburn, M. Danzig, H. Hubinger, D. Soisson, and H. P. Schultz, *J. Org. Chem.*, **26**, 2805 (1961).

(6) R. W. Holley and A. D. Holley, *J. Amer. Chem. Soc.*, **74**, 1110, 5445 (1952).

(7) L. Horner, U. Schwenk, and E. Junghanns, *Justus Liebigs Ann. Chem.*, **579**, 220 (1953).

(8) K. L. Kirk and L. A. Cohen, *J. Org. Chem.*, **34**, 395 (1969), and many references in all above.

(9) R. Van Dusen and H. P. Schultz, *ibid.*, **21**, 1326 (1956).

column. Curiously, **3** was stable in boiling water, but not in boiling organic solvents!

Reduction of **3** to **4** was effected with $LiAlH_4$ in dioxane. Aliquot portions of the reaction solution, monitored for disappearance of the carbonyl peak in the ir spectrum, indicated 12 hr as the optimum reduction time. Similar reduction executed in THF required longer reaction times (24–48 hr) and resulted in considerable racemization of the active isomer. Reduction did not occur in diethyl ether, contrary to what was expected in light of the findings of Smith, Rebel, and Beach.[10]

Compound **4** was smoothly hydrogenolyzed to **5** by Pd–C catalyst in $KHCO_3$–EtOH solution.

Several experiments shortened the work required for the transformation of **2** into **5** without isolation of the intermediate compounds by executing chemical and catalytic reductions one after the other in the appropriate solvent. Although analytically pure *R*-**5** and *S*-**5** were thus obtained, optical activities indicated that extensive racemization of the compounds had occurred.

The optical antipode (*R*-**5**) of *S*-**5** was prepared by resolution of *RS*-**5**[11] (obtained by catalytic reduction of 2-methylquinoxaline[12]) with dibenzoyl-*d*-tartaric acid.[13] *R*-**5** possessed optical activity virtually identical with (but of opposite sign) the unequivocally prepared *S*-**5**, indicating that racemization of *S*-**5** did not occur to a significant extent during its synthesis. This resolution, the consequence of the fortuitous circumstance that the dibenzoyl derivative of readily available *d*-tartaric acid effected isolation of *R*-**5** from *RS*-**5**, provided a source of *R*-**5** which avoided its lengthy unequivocal synthesis with the attendant demand for costly D-α-alanine as starting material.

Experimental Section[14]

N-(2-Nitro-5-bromophenyl)-α-alanine (2).—A warm (60°) solution of 36 g (0.4 mol) of α-alanine, 40 g (0.4 mol) of $KHCO_3$, and 125 ml of H_2O was added dropwise in 0.5 hr to a refluxing solution of 113 g (0.4 mol) of 2,4-dibromonitrobenzene[9] in 500 ml of 95% EtOH; the homogeneous solution was refluxed for 48 hr. Filtration, concentration to 250 ml, addition of 300 ml of H_2O, and again filtration afforded 68 g (60.2%) of recovered 2,4-dibromonitrobenzene. After clarification with decolorizing carbon, the filtrate was brought to pH 1 with HCl to give 50.4 g (42.2%) of crude **2**, mp 161–166°. The solid was dissolved in 300 ml of 1 *N* NH_4OH, clarified, reprecipitated with HCl, and then recrystallized from C_6H_6 (40 ml/g) to give 42.3 g (35.5%) of yellow plates.

S-**2**: 35%; mp 188–189°; uv max 205 mμ (ε 12,000), 241 (19,300), 289 (7300), 412 (6500); ir (KBr) 3340 (NH), 1720 (C=O), 480 cm^{-1} (CBr); $[\alpha]^{24}D$ +8.91° (*c* 1.0, THF), +47.0° (*c* 1.5, 95% EtOH), +60.0° (*c* 1.2, HOAc).

Anal. Calcd for $C_9H_9BrN_2O_4$: C, 37.39; H, 3.14; Br, 27.64; N, 9.69. Found: C, 37.60; H, 3.00; Br, 27.70; N, 9.70.

RS-**2**: 38.5%; mp 174–175° (lit.[9] 175–177°); uv and ir same as *S*-**2**.

R-**2**: 33.5%; mp 186.5–187.5°; mmp (*R*-**2** and *S*-**2**) 174–176°; $[\alpha]^{27}D$ −8.00° (*c* 2.5, THF), −59.0° (*c* 1.5, HOAc); uv and ir same as *S*-**2**. *Anal.* Found: C, 37.60; H, 3.38; Br, 27.95; N, 9.81.

3-Methyl-6-bromo-3,4-dihydro-2(1H)-quinoxalinone (3). Method A ($SnCl_2$ Reduction).—A solution of 11.5 g (0.04 mol) of **2** in 250 ml of 95% EtOH was mixed with a solution of 45.2 g (0.2 mol) of $SnCl_2 \cdot 2H_2O$ in 400 ml of EtOH–12 *N* HCl (1:1) and stirred until colorless (40 hr) in a sealed desiccator initially evacuated to 10 mm. After concentration *in vacuo* to 100 ml, 200 ml of H_2O was added and the mixture was cooled at 0° and filtered. The moist product was thoroughly washed with water (otherwise the material obtained is a $SnCl_x$ complex of the quinoxalinone) and dried to give 7.24 g (75%) of white needles. Recrystallization from hot water (55 ml/g) with filtration through glass wool gave 6.35 g (66%) of solid; again recrystallization by dissolving in cold (24°) $CHCl_3$ (10 ml/g) and, after treatment with decolorizing carbon and Filter Aid, addition of ligroin (bp 66–75°, 10 ml/g) and cooling at 0° gave 5.32 g (55%) of white fibrous needles.

S-**3**: 42%; mp 132.5–133.5°; uv max 229 mμ (ε 39,400), 274 (4000), 315 (6300); ir (KBr) 3375, 3400 (NH), 1676 (C=O), 490 cm^{-1} (CBr); pmr ($CDCl_3$) δ 1.38 (d, *J* = 7 Hz, 3 H, CH_3), 3.98 (m, 2 H, CH and NH), 6.74 (m, 3 H, aromatic), 9.63 (broad s, 1 H, CONH), multiplet at 3.98 became a quartet (*J* = 7 Hz) upon exchange with D_2O; $[\alpha]^{24}D$ +59.8° (*c* 1.0, THF), +63.7° (*c* 0.9, HOAc), +71.3° (*c* 1.0, 95% EtOH).

Anal. Calcd for $C_9H_9BrN_2O$: C, 44.84; H, 3.76; N, 11.62. Found: C, 45.07; H, 3.68; N, 11.77.

RS-**3**: 55%; mp 128–130°; uv, ir, and pmr same as *S*-**3**. *Anal.* Found: C, 44.60; H, 3.84; N, 11.60.

Method B (Raney Nickel Reduction).—A mixture of 0.43 g (1.5 mmol) of **2**, 0.7 g (7 mmol) of $KHCO_3$, and 3 g of W-2 Raney nickel catalyst[15] in 20 ml of water was reduced at 47 psi for 3 hr at 24° until the orange color disappeared. The mixture was filtered into an equivalent amount of 1 *N* HCl, cooled, and filtered to give 0.18 g (50%) of tan solid, mp 123–126°. Recrystallization of the crude material as above gave 0.12 g (33%) of white crystals of constant melting point.

S-**3**: 33%; mp 130–132°; the mixture melting point with sample prepared by $SnCl_2$ reduction gave no depression; $[\alpha]^{24}D$ +57.3° (*c* 1.0, THF).

RS-**3**: 31.5%; mp 128–130°; mixture melting point with sample prepared by $SnCl_2$ reduction gave no depression.

Method C (Palladium Reduction).—A solution of 2.89 g (0.01 mol) of **2** in 25 ml of THF was reduced over 1 g of 10% Pd–C catalyst[16] at 40 psi and 30° for 12 hr until colorless. Filtration and removal of the solvent under vacuum, 40°, gave an oily residue which was dissolved in 10 ml of hot Me_2CO, treated with decolorizing carbon and Filter Aid, filtered, and diluted with 40 ml of ligroin (bp 60–90°). After cooling at 0°, 1.4 g (58%) of white crystals were obtained, mp 126–128°. Two recrystallizations from Me_2CO–ligroin (1:5, 40 ml/g) gave 1.2 g (50%) of white platelets of constant melting point.

S-**3**: 50%; mp 131–132.5°; uv and ir, as above; $[\alpha]^{27}D$ +52.0° (*c* 2.0, THF), +61.8° (*c* 2.5, HOAc). *Anal.* Found: C, 44.85; H, 4.05; N, 11.63.

R-**3**: 50%; mp 131–132.5°; uv and ir, as above; $[\alpha]^{27}D$ −52.9° (*c* 2.0, THF), −61.1° (*c* 2.5, HOAc); mmp (*S*-**3** and *R*-**3**) 126–127°. *Anal.* Found: C, 45.08; H, 3.47; N, 11.70.

2-Methyl-7-bromo-1,2,3,4-tetrahydroquinoxaline (4).—A mixture of 1.19 g (4.9 mmol) of **3** and 0.76 g (20 mmol) of $LiAlH_4$ in 30 ml of dry dioxane was refluxed 12 hr with stirring under N_2. After the solution was cooled in an ice bath, excess $LiAlH_4$ was destroyed by successive dropwise addition of 0.75 ml of H_2O, 0.55 ml of 20% NaOH, and 2.6 ml of H_2O. After 1–2 hr of stirring, the solid was filtered and the filtrate was evaporated to dryness. The residue from evaporation was dissolved in 40 ml of $CHCl_3$, treated with decolorizing carbon and Filter Aid, and then extracted three times with 20-ml portions of 1 *N* HCl and once with 5 ml of 6 *N* HCl. The acid extracts were clarified, basified with 6 *N* NaOH, cooled, and filtered to give 0.67 g (60%) of tan solid. Three recrystallizations from hot ligroin (bp 66–75°) (50 ml/g) gave shiny white plates of constant melting point.

S-**4**: 33%; mp 131–132° dec; uv max 225 mμ (ε 27,000),

(10) R. F. Smith, W. J. Rebel, and T. N. Beach, *J. Org. Chem.*, **24**, 205 (1959).

(11) M. Munk and H. P. Schultz, *J. Amer. Chem. Soc.*, **74**, 3433 (1952).

(12) K. Bottcher, *Ber.*, **46**, 3085 (1913).

(13) C. L. Butler and L. H. Cretcher, *J. Amer. Chem. Soc.*, **55**, 2605 (1933). M. Semonsky, A. Cerny, and V. Zikan, *Chem. Listy*, **50**, 116 (1956); *Collect. Czech. Chem. Commun.*, **21**, 382 (1956); *Chem. Abstr.*, **50**, 13059*a* (1956).

(14) Uv absorption spectra were obtained from samples at concentrations of 5 mg/l. of 95% EtOH with a Bausch and Lomb Spectronic 505 spectrophotometer using 1-cm silica cells. H nmr spectra, all referred to internal TMS, were determined on a Hitachi Perkin-Elmer R-20 spectrometer at 60 MHz, 34°; the δ values for multiplets were taken at the center of gravity. All optical activities were observed on a Rudolph Model 63 polarimeter. Melting points, determined on a Thomas–Hoover apparatus, were uncorrected. Elemental analyses were performed by Peninsular ChemResearch, Gainesville, Fla.

(15) R. Mozingo, *Org. Syn.*, **21**, 15 (1941).

(16) Aceto Chemical Co., Inc., Flushing, N. Y.

268 (4500), 324 (4500); ir (KBr) 3320 (NH), 455 cm^{-1} (CBr); pmr ($CDCl_3$) δ 1.18 (d, J = 6.5 Hz, 3 H, CH_3), 2.8–3.8 (m, 5 H, CH, CH_2, NH), 6.5 (m, 3 H, aromatic); $[\alpha]^{24}D$ +13.0° (*c* 1.0, THF).

Anal. Calcd for $C_9H_{11}BrN_2$: C, 47.60; H, 4.88; N, 12.33. Found: C, 47.74; H, 4.99; N, 12.41.

RS-**4**: 25.5%; mp 156.5–158°; uv and ir same as *S*-**4**; pmr (acetone-d_6) δ 1.12 (d, J = 6.5 Hz, 3 H, CH_3), 2.87 (s, 1 H, NH), 2.9–3.4 (m, 3 H, CH_2, CH), 4.81 (broad s, 1 H, NH), 6.52 (m, 3 H, aromatic), the broad singlets at 2.87 and 4.81 disappear upon exchange with D_2O. *Anal.* Found: C, 47.90; H, 5.07; N, 12.41.

N,N′-Diacetyl-2-methyl-7-bromo-1,2,3,4-tetrahydroquinoxaline.—In 1 ml (10 mmol) of Ac_2O was dissolved 0.24 g (1 mmol) of compound **4**. After 24 hr at 24°, 1 ml of H_2O was added to the reaction solution which was clarified, filtered, and evaporated to dryness to give 0.27 g (87%) of yellow crystals. Three recrystallizations from ligroin (bp 66–75°, 40 ml/g) gave 0.23 g (74%) of white crystals of constant melting point.

S derivative: 74%; mp 131–132.5°; uv max 234 mμ (ϵ 39,000), 258 (15,000); ir (KBr) 1656 (C=O), 496 cm^{-1} (CBr); pmr ($CDCl_3$) δ 1.14 (d, J = 6.5 Hz, 3 H, CH_3), 2.19 (s, 6 H, $COCH_3$), 2.7–3.3 (m, 1 H, CH), 4.5–5.3 (m, 2 H, CH_2), 7.48 (m, 3 H, aromatic); $[\alpha]^{24}D$ +29.9° (*c* 1.1, THF).

Anal. Calcd for $C_{13}H_{15}BrN_2O_2$: C, 50.18; H, 4.86; N, 9.00. Found: C, 50.07; H, 4.83; N, 9.04.

RS derivative: 75%; mp 129–130°; uv, ir, and pmr same as *S* derivative. *Anal.* Found: C, 50.19; H, 4.85; N, 8.96.

2-Methyl-1,2,3,4-tetrahydroquinoxaline (**5**).—A mixture of 0.12 g (0.53 mmol) of **4**, 0.1 g (1 mmol) of $KHCO_3$, and 0.1 g 10% Pd–C catalyst in 20 ml of 95% EtOH was hydrogenated for 20 hr at 46 psi and 24°. After removal of the catalyst, the filtrate was evaporated to dryness, and the solid residue extracted two times with 10-ml portions of hot ligroin (bp 66–75°). The hot extracts were clarified, cooled, and filtered to give 0.05 g (64%) of yellow solid. Two recrystallizations from hot ligroin (bp 66–75°, 20 ml/g) gave white plates of constant melting point.

S-**5**: 40%; mp 90–90.5°; uv max (95% EtOH) 220 mμ (ϵ 25,700), 258 (2960), 311 (2960); uv max (0.1 *N* HCl) 210 (6600), 243 (5160), 294 (1300); ir (KBr) 3310, 3355 cm^{-1} (NH); pmr ($CDCl_3$) δ 1.10 (d, J = 6 Hz, 3 H, CH_3), 2.7–3.5 (m, 3 H, CH_2, CH), 3.51 (s, 2 H, NH), 6.54 (m, 4 H, aromatic), singlet at 3.51 disappears upon exchange with D_2O; $[\alpha]^{24}D$ +60.2° (*c* 1.0, THF), −6.1° (*c* 1.0, $CHCl_3$), −35.8° (*c* 1.0, 95% EtOH).

Anal. Calcd for $C_9H_{12}N_2$: C, 72.94; H, 8.16; N, 18.90. Found: C, 72.78; H, 8.08; N, 18.78.

RS-**5**: 34%; mp 70–71° (lit.[11,17] mp 70–71°; lit.[18] 71°); uv, ir, and pmr same as *S*-**5**.

(17) C. Ris, *Ber.*, **21**, 383 (1888).

(18) S. Maffei and S. Pietra, *Gazz. Chim. Ital.*, **88**, 562 (1958).

R-**5**: prepared by a continuous sequence of reactions involving *R*-**2**, *R*-**3**, and *R*-**4** including THF–$LiAlH_4$ reduction to *R*-**4**, without any isolation or purification steps; 20%; mp 73–74°; uv and ir same as *S*-**5**; $[\alpha]^{27}D$ −3.8° (*c* 2.0, THF). *Anal.* Found: C, 72.80; H, 7.93; N, 19.02.

R-**5**: prepared by resolution of *RS*-**5**. To a solution of 7.52 g (20 mmol) of dibenzoyl-*d*-tartaric acid[13] in 35 ml of C_6H_6–95% EtOH (4:1) was added a solution of 2.96 g (20 mmol) of *RS*-**5**[11] in 20 ml of C_6H_6. After 12 hr at 24°, 5.16 g (44.1%) of white solid, mp 149–153°, $[\alpha]^{24}D$ −63.2° (*c* 1.0, 95% EtOH), was obtained. Three recrystallizations from hot Me_2CO (4 ml/g) solution poured into hot C_6H_6 (5 ml/g) gave 2.75 g (23.5%) of material of constant melting point and [α] that analyzed for the monobenzene solvated 1:1 salt, mp 150–151°, $[\alpha]^{24}D$ −60.0° (*c* 1.0, 95% EtOH).

Anal. Calcd for $C_9H_{12}N_2 \cdot C_{18}H_{14}O_8 \cdot C_6H_6$: C, 67.80; H, 5.52; N, 4.79. Found: C, 67.56; H, 5.65; N, 4.89.

Addition of 10 ml of 1 *N* NaOH to the salt, followed by filtration, gave 0.55 g (37.2% yield of total *R*-**5** isomer initially present), mp 90–91°, $[\alpha]^{24}D$ +31.7° (*c* 1.0, 95% EtOH). Two recrystallizations from ligroin (20 ml/g) gave 0.32 g (21.6%) of material of constant melting point and [α]: mp 90.5–91°; $[\alpha]^{24}D$ −60.3° (*c* 1.0, THF), +6.07° (*c* 1.0, $CHCl_3$), +35.1° (*c* 1.0, 95% EtOH); uv, ir, and pmr, same as *S*-**5**. *Anal.* Found: C, 72.75; H, 8.33; N, 18.92.

N,N′-Diacetyl-2-methyl-1,2,3,4-tetrahydroquinoxaline.—This was prepared and purified as was the related bromo compound above.

S derivative: 82.5%; mp 143–144°; uv max 226 mμ (ϵ 23,200), 251 (12,300); ir (KBr) 1645 cm^{-1} (C=O); pmr ($CDCl_3$) δ 1.15 (d, J = 6 Hz, 3 H, CH_3), 2.18 and 2.21 (2 s, 6 H, $COCH_3$), 2.4–3.2 (m, 1 H, CH), 4.5–5.3 (m, 2 H, CH_2), 7.34 (m, 4 H, aromatic); $[\alpha]^{24}D$ +133.2° (*c* 1.0, THF).

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.23; H, 6.90; N, 12.13.

RS derivative: 76.5%; mp 141–143° (lit.[18] mp 138–139°); uv, ir and pmr same as *S* derivative.

Registry No.—*R*-**2**, 24463-23-8; *S*-**2**, 24463-22-7; *R*-**3**, 24463-24-9; *RS*-**3**, 24463-25-0; *S*-**3**, 24463-26-1; *RS*-**4**, 24463-27-2; *S*-**4**, 24515-51-3; *R*-**5**, 24463-30-7; *S*-**5**, 24463-31-8; N,N′-diacetyl-2-methyl-7-bromo-1,2,3,4-tetrahydroquinoxaline, *S* derivative, 24463-28-3; N,N′-diacetyl-2-methyl-7-bromo-1,2,3,4-tetrahydroquinoxaline, *RS* derivative, 24463-29-4; N,N′-diacetyl-2-methyl-1,2,3,4-tetrahydroquinoxaline, *S* derivative, 24463-32-9.