After workup and chromatography on silica gel (20% ether–hexanes), 241 mg (57%) of alcohol **21** was obtained as a 75:25 mixture of erythro and threo isomers: IR film ν 3400, 2940, 2865, 2840, 1640, 1470, 1260, 1105 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, CH_3Si), 0.91 (s, *tert*-butyl), 1.23–1.38, 1.41–1.50, 1.51–1.67 (m, CH_2's), 1.73 (p, J = 6 Hz, $CH_2CH_2CH_2$), 1.83 (d, J = 6 Hz, OH), 2.10–2.18 (m, threo allylic CH), 2.26–2.34 (m, erythro allylic CH), 2.53–2.64 (m, allylic CH_2's), 2.56–2.66 (m, CH_2OSi), 4.12–4.8 (m, threo carbinyl CH), 4.22–4.28 (m, erythro carbinyl CH), 5.08–5.25 (m, vinyl H's), 5.53–5.72 (m, vinyl H's); MS, calcd for $C_{24}H_{49}O_3Si_2I$ m/e 568.7, found m/e ($M^+ - C(CH_3)_3$) 511. Anal. Calcd for $C_{24}H_{49}O_3Si_2I$: C, 50.69; H, 8.68. Found: C, 50.79; H, 8.70.

Acknowledgment. Support from the National Institute of General Medical Sciences through Research Grant 2RO1-GM29475 is gratefully acknowledged. A generous gift of geraniol was kindly provided by Dr. Alan Hochstetler, Givaudan Corporation, Clifton, NJ. We thank the South Carolina Regional Nuclear Magnetic Resonance Center for cooperation in securing high-field NMR spectra.

An Asymmetric Synthesis of (+)-Morphinans in High Enantiomeric Purity

A. I. Meyers* and Thomas R. Bailey

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

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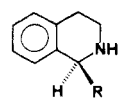
The synthesis of the narcotic analgesic dextrorphan (**4**) and its desoxy derivative has been accomplished via an asymmetric alkylation of octahydroisoquinoline **10**. The latter, converted to its chiral formamidine **13**, underwent highly selective alkylation to give the 1-benzyl derivative **16** in >98% ee. Grewe cyclization then produced the title compounds.

In the continuing study on chiral formamidines, as precursors to α-lithio anions, which have thus far led to asymmetric synthetic methods for tetrahydroisoquinolines **1**,[1] β-carbolines **2**,[2] piperidines and pyrrolidines **3**, and



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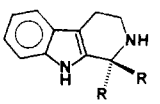

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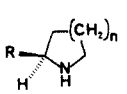

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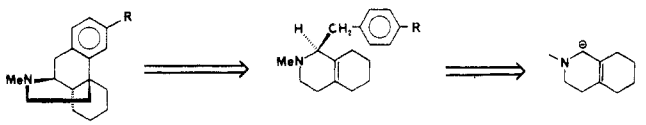
benzomorphans,[3,4] we describe an efficient synthesis of morphinans which includes the preparation of dextrorphan (**4**) and its unsubstituted derivative. These substances

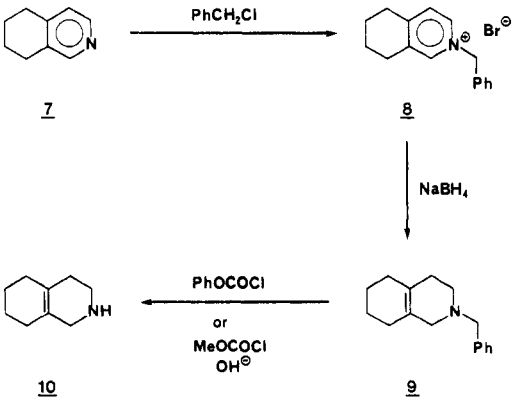


4, R = H, OH **5** **6**

have been the subject of considerable effort over the past 35 years due to their analgesic and antitussive properties. Synthetic approaches to the morphine-based system have also enjoyed considerable success[5] and continue even in recent years.[6] However, there are no reported asymmetric syntheses to these systems and it is the purpose of this paper to disclose a successful entry into enantiomercially enriched (>98%) morphinans.

Our approach is to generate a chiral carbanion from the octahydroisoquinoline **6** via formamidines and to alkylate, in a stereoselective manner, to the benzyl derivative **5**. The final construction to the morphinan **4** makes use of the well-known Grewe cyclization[7] under acidic condtions.

The synthetic scheme begins with the acquisition of the octahydroisoquinoline (**10**), which was prepared in 30–40% overall yield from isoquinoline. The latter was reduced[8] with hydrogen–palladium–trifuloroacetic acid to the tetrahydroisoquinoline **7** followed by quaternization with benzyl bromide to furnish the *N*-benzyl salt **8**. Reduction



7 **8** **9** **10**

with sodium borohydride gave the *N*-benzyloctahydroisoquinoline **9**, which was debenzylated to 1,2,3,4,5,6,7,8-octahydroisoquinoline (**10**). Transformation into the chiral

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(5) (a) Eddy, N. B.; May, E. L. "Synthetic Analgesics, Part 2"; Pergamon Press: London, 1966. (b) Palmer, D. C.; Strauss, M. J. *Chem. Rev.* **1977**, *77*, 1. (c) Lednicer, D.; Mitscher, L. A. "Organic Chemistry of Drug Synthesis"; Wiley-Interscience: New York, 1977.

(6) Evans, D. A.; Mitch, C. H.; Thomas, R. C.; Zimmerman, D. M.; Robey, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 5955. Monkovic, I.; Bachand, C.; Wong, H. *J. Am. Chem. Soc.* **1978**, *100*, 4609.

(7) Grewe, R.; Mondon, A. *Chem. Ber.* **1948**, *81*, 279. For a detailed discussion on the Grewe cyclization, see ref 5b above.

(8) Vierhapper, F. W.; Eliel, E. L. *J. Org. Chem.* **1975**, *40*, 2729.

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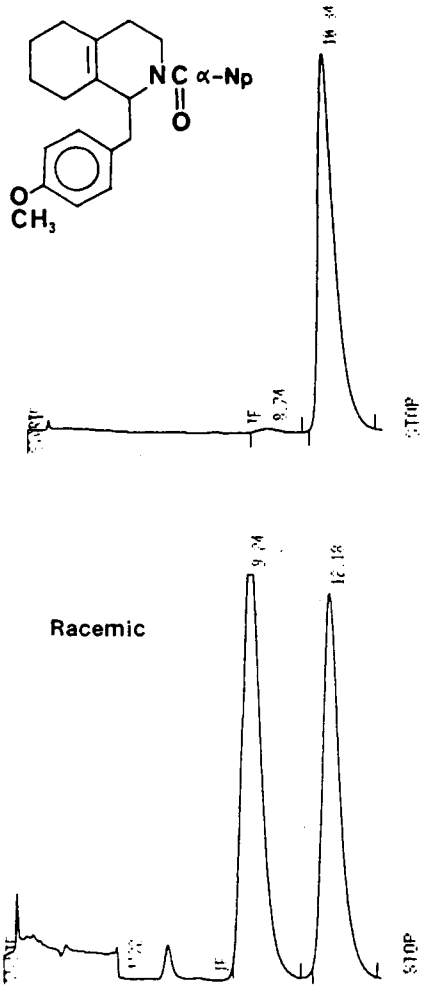
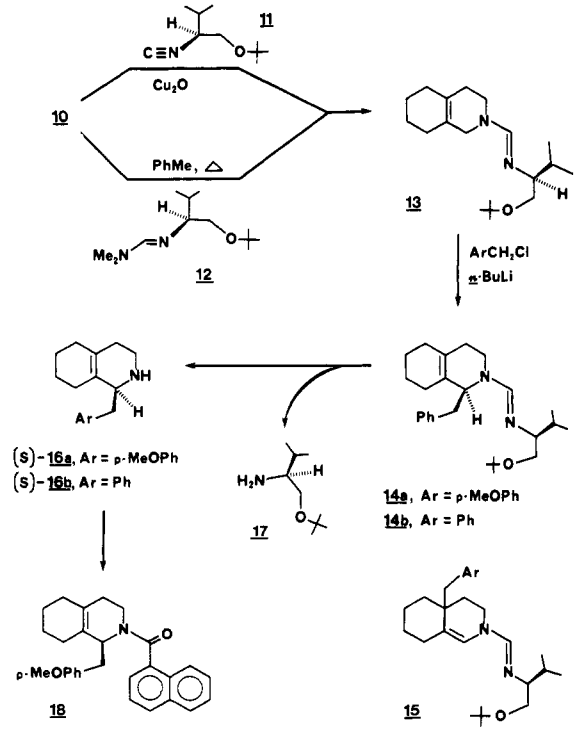


Figure 1. Pirkle column analysis of racemic **18** and (−)-**18**. Ratios are 98.87 to 1.13 (98% ee).

formamidine **13** was accomplished by treating the octahydroisoquinoline **10** with the isocyanide derived from valinol *tert*-butyl ether **11**, in the presence of cuprous

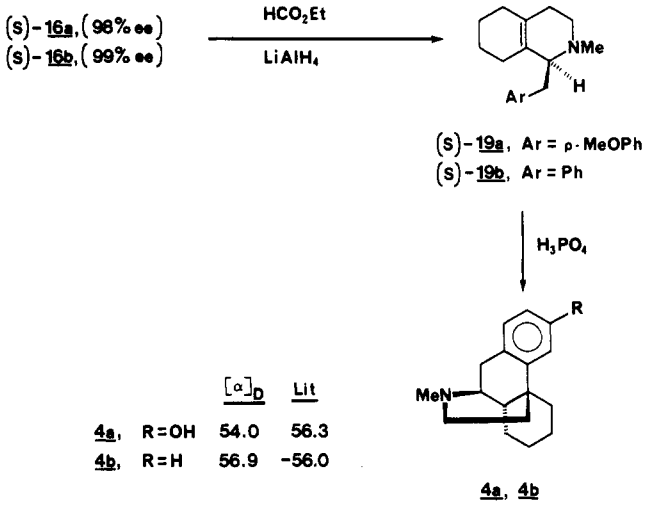


oxide, or the dimethyl formamidine **12**[3] by simple heating to eliminate dimethylamine. Although the isocyanide–amine addition to **13** works well (~70%), it was found that for larger scale reactions the (dimethylamino)formamidine **12** gave more consistent yields (~80%). The isocyanide gave lower yields of **13** as the reactions were scaled up.

With the octahydroisoquinoline–valineformamidine in hand, the sequence to the morphinans proceeded by metalation–alkylation of **13** to give the benzylated derivatives **14** and **15**. The ratio of 1- vs. 5-benzylation with benzyl chloride was 4:1, respectively, while *p*-methoxybenzyl chloride gave a 7:1 ratio for **14** and **15**. It was unnecessary to separate **14** from **15** since the next step, which involved hydrazinolysis, selectively destroyed **15** such that the only product isolated was the 2-benzyloctahydroisoquinoline **16a** or **16b**. Also isolated during the hydrazine treatment was a 75% recovered yield of the *tert*-butyl ether of valinol **17**.

In order to assess the enantiomeric purity of the benzyloctahydroisoquinolines **16a**, **16b**, they were transformed into their naphthamides **18** and subjected to HPLC analysis utilizing the chiral Pirkle column.[9] A typical separation is shown in Figure 1. Integration of these peaks showed that **16a** and **16b** were formed in 99% and 98.5% ee, respectively.

Treatment of **16a** and **16b** with ethyl formate followed by lithium aluminum hydride reduction gave the *N*-methyl derivatives **19a** and **19b** in 82–90% yield, which were then



subjected to hot phosphoric acid under Grewe conditions,[7] affording the morphinans **4a**, **4b** in 45–50% yield. Comparison of these products with the literature values showed that the optical purities were 99% and 96%, respectively, in agreement with the HPLC enantiomeric analysis.

In summary, we have demonstrated an efficient asymmetric synthesis of morphinans in high enantioselectivity, and this, coupled with the benzomorphan synthesis already described, provides a route into a wide variety of morphine-based alkaloids.

Experimental Section

The NMR spectra were determined on a Bruker-IBM 270 MHz instrument. Optical rotations were taken on a Rudolph AutoPol polarimeter. The HPLC analyses were performed on a Waters 440 unit with flow rates of 3.0 mL/min. The Pirkle column was a Baker (J. T. Baker and Co.) dinitrophenylglycine covalent HPLC column (No. RP-71130), using 5% isopropyl alcohol in hexane as the eluent.

***N*-Benzyl-5,6,7,8-tetrahydroisoquinolinium Bromide (8).** A solution of 10.0 g (7.7 mmol) of distilled isoquinoline in 67 mL

(9) Pirkle, W. H.; Welch, C. J.; Mahler, G. S.; Meyers, A. I.; Fuentes, L. M.; Boes, M. *J. Org. Chem.* **1984**, *49*, 2504.

of trifluoroacetic acid containing 5.0 g of 5% palladium on carbon was hydrogenated in the manner of Eliel and Vierhapper[8] at 50 psi of H_2, 50 °C over 48 h. The catalyst was removed by filtration, and the reaction mixture was carefully neutralized with solid KOH and 20% KOH solution. Extraction with CH_2Cl_2, followed by a saturated $NaHCO_3$ solution wash, afforded, upon concentration, 10.0 g of the crude product contaminated with some overreduced material. The crude 5,6,7,8-tetrahydroisoquinoline was dissolved in 70 mL of reagent grade acetone, 10.3 mL (8.7 mmol) of benzyl bromide was added, and the solution was refluxed for 1 h. Upon cooling, the benzyl bromide salt precipitated from solution as a fine white powder. Filtration provided 16.9 g (72%) of the product. Recrystallization from methanol/ether afforded large prisms: mp 185–186 °C (uncorrected), lit.[10] ml 178–180 °C.

***N*-Benzyl-1,2,3,4,5,6,7,8-octahydroisoquinoline (9).** To a solution of 4.0 g (1.3 mmol) of the pyridinium benzyl bromide **8** in 25 mL of 80% aqueous methanol at 0 °C was slowly added 1.0 g (2.6 mmol) of $NaBH_4$. After completion of the addition, the reaction mixture was refluxed for 1 h. Upon cooling, the methanol was removed in vacuo, and the crude product was taken up in ether and washed with saturated $NaHCO_3$ solution, and the organic layer was dried over K_2CO_3. Bulb-to-bulb distillation at 90 °C (0.05 mmHg) provided 2.8 g (93%) of the product as a colorless liquid: ^1H NMR ($CDCl_3$) δ 1.8 (10 H, m), 2.5 (2 H, t, J = 5 Hz), 2.8 (2 H, m), 3.6 (2 H, s), 7.3 (5 H, s); mp (oxalate salt) 179–181 °C, lit.[10] mp 183 °C.

1,2,3,4,5,6,7,8-Octahydroisoquinoline (10). To a solution of 2.826 g (0.024 mol) of the *N*-benzyl-1,2,3,4,5,6,7,8-octahydroisoquinoline in 40 mL of CH_2Cl_2 was carefully added 2.4 mL (2.5 equiv) of methyl chloroformate (or phenyl chloroformate). After 2 h, the reaction mixture was concentrated in vacuo, and the benzyl chloride generated from the reaction was removed by bulb-to-bulb distillation. The crude urethane was then dissolved in 40 mL of THF containing 5 mol % of 18-crown-6. To this mixture was added 2 g (3 equiv) of powdered KOH and the reaction mixture was refluxed under argon for 2 days. Upon cooling, the solvent was removed in vacuo, and the crude material was taken up in diethyl ether. The ethereal phase was washed with saturated $NaHCO_3$ solution 3 times and the organic layer was dried over anhydrous K_2CO_3. Bulb-to-bulb distillation (20 mmHg; 105 °C) provided 0.995 g (60%) of the product as a colorless liquid: ^1H NMR ($CDCl_3$) δ 1.9 (11 H, m), 3.0 (2 H, t, J = 5 Hz), 3.2 (2 H, m).[8] Anal. Calcd for $C_9H_{15}N$: C, 78.88; H, 11.02. Found: C, 78.97; H, 11.09. Picrate prepared in ethanol, mp 169–170 °C; hydrochloride (MeOH–ether) mp 147–149 °C.

Valineformamidine of Octahydroisoquinoline 10. A solution of 0.560 g (4.1 mmol) of 1,2,3,4,5,6,7,8-octahydroisoquinoline (**10**) and 0.860 g (4.0 mmol) of (*S*)-*N*,*N*-dimethyl-*O*-*tert*-butylvalinolformamidine **12**[3] in 1 mL of toluene was heated at 85 °C for 48 h. Concentration and flash chromatography (silica gel; 5% Et_3N in hexanes) of the crude product afforded 0.998 g (80%) of the product as a colorless oil: IR (film) 2920 (br), 2820, 1640, 1450, 1385, 1355, 1230, 1190, 1075, 1010, 875 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (6 H, d, J = 7 Hz), 1.15 (9 H, s), 1.59 (4 H, m), 1.88 (7 H, m), 2.70 (1 H, q, J = 6 Hz), 3.18 (1 H, m), 3.30 (2 H, t, J = 6 Hz), 3.55 (3 H, m), 7.31 (1 H, s); $[\alpha]^{24}_D$ −44.6° (*c* 3.3, $CHCl_3$). Elemental analyses were not taken due tot he ready absorption of oxygen, carbon dioxide, and water. These formamidines are best stored under argon after degassing under high vacuum.

Isocyanide of (*S*)-Valinol *tert*-Buyl Ether (11). *N*-Formylvalinol t-butyl ether[3] (8.52 g) was dissolved in 50 mL of dry DMF and then cooled to −50 °C, and a solution of 5.4 g of thionyl chloride, dissolved in 20 mL of DMF, was added. After the addition was complete the solution was warmed to −30 °C and was recooled to −50 °C. While the solution was stirring at −50 °C, 9.6 g of solid K_2CO_3 was added. The colorless mixture was allowed to warm to room temperature overnight. Extraction of the crude material was done by partitioning it between H_2O and ether and drying the combined organic layers with $MgSO_4$. The crude product was distilled, bulb-to-bulb at 78 °C (3 torr), yielding 6.5 g of the isonitrile, 85%: ^1H NMR ($CDCl_3$) δ 3.45 (3 H, m), 1.22 (9 H, s), 1.05 (3 H, J = 7 Hz, d), 1.00 (3 H, J = 7 Hz, d); IR (neat 2940, 2120 cm^{-1}; $[\alpha]^{24}_D$ +1.76° (*c* 1.19, $CHCl_3$). Anal. Calcd for $C_{10}H_{19}NO$: C, 71.00; H, 11.24. Found: C 69.89; H, 11.19.

Valineformamidine 13 from Isocyanide 11. A solution of 0.560 g (4.1 mmol) of 1,2,3,4,5,6,7,8-octahydroisoquinoline and 0.69 g (4.1 mmol) of (*S*)-*O*-*tert*-butylvalinol isocyanide in 10 mL of toluene was heated at reflux for 16 h with a catalytic amount of dry cuprous oxide. Concentration and flash chromatography (silica gel; 5% Et_3N in hexanes) of the crude product afforded 0.87 g (70%) of the product as a colorless oil whose spectral data, $[\alpha]_D$, and other physical properties were identical with **13** prepared from **12**.

1-(*p*-Methoxybenzyl)-1,2,3,4,5,6,7,8-octahydroisoquinolineformamidine (14a). To a 0.05 M solution of 0.221 g (0.721 mmol) of the chiral octahydroisoquinolineformamidine **13** and 0.22 mL (2 equiv) of *p*-methoxybenzyl chloride in THF at −78 °C, under argon, was added 1.1 equiv of *n*-butyllithium in hexane. The light yellow solution had become completely colorless after 1 h, and after an additional hour at −78 °C, the reaction mixture was allowed to warm to 0 °C. The reaction mixture was poured into hexane, and the organic layer was washed with 1 N HCl solution. After separation of the layers, excess *p*-methoxybenyl chloride could be recovered from the hexane/THF layer. The acid wash was made basic with 20% KOH solution, and the milky white aqueous phase was extracted with diethyl ether several times. Concentration and passage of the crude product through a small silica gel plug and elution with 5% Et_3N in hexanes ("flash filtration") provided 0.281 g (92%) of a 7:1 ratio of 1- vs. 5-substituted regioisomers (**14a**, **15**). If desired, radial chromatography of this mixture on a 2-mm silica gel plate, eluting with 5% Et_3N in hexanes, separated the regioisomers, affording 0.203 g (66%) of the 1-(*p*-methoxybenzyl)octahydroisoquinolineformamidine **14a** as a clear, viscous oil: IR (film) 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (6 H, m), 1.10 (9 H, s), 1.60 (6 H, m), 1.86 (4 H, m), 2.10 (2 H, m), 2.60 (1 H, m), 2.90 (4 H, m), 3.41 (1 H, m), 3.76 (4 H, 2 s and m), 6.76 (2 H, m), 7.05 (3 H, m). This product was carried on directly to the hydrazine treatment.

(*S*)-1-(*p*-Methoxybenzyl)-1,2,3,4,5,6,7,8-octahydroisoquinoline (16a). A solution of 0.438 g (1.03 mmol) of the 1-(*p*-methoxybenzyl)octahydroisoquinolineformamidine **14a** in 7 mL of 95% EtOH, 0.27 mL (8 equiv) of hydrazine, and 0.18 mL of glacial acetic acid was heated at 50 °C under argon for 12 h. Upon cooling, the reaction mixture was taken up in diethyl ether, and the organic phase was washed with 20% KOH solution and dried over anhydrous K_2CO_3. Concentration under aspirator pressure (cold!) followed by bulb-to-bulb distillation at 80 °C (20 mmHg) afforded 0.127 g (75%) of the *tert*-butyl ether of (*S*)-valinol (**17**). Subsequent bulb-to-bulb distillation of the pot residue (0.05 mmHg, 110 °C) provided 0.214 g (81%) of the chiral secondary amine a a viscous, colorless oil: ^1H NMR ($CDCl_3$) δ 1.64 (5 H, m), 1.92 (6 H, m), 2.75 (5 H, complex multiplets), 3.78 (3 H, s), 6.84 (2 H, d, J = 8 Hz), 7.14 (2 H, d, J = 8 Hz); $[\alpha]^{24}_D$ −175.8° (*c* = 1.7 ether). The enantiomeric excess was determined on the α-naphthamide whose preparation follows.

α-Naphthamide 18. General Procedure. A stirred dichloromethane solution containing **16a** or **16b** (0.1 m) was treated with 5 equiv of triethylamine at room temperature. α-Naphthoyl chloride (1.5 equiv) was added and the mixture was stirred under dry nitrogen overnight. The solution was partitioned between dichloromethane and 10% aqueous KOH (1:1) and the aqueous layer separated. The aqueous phase was extracted (2 × 50 mL) with dichloromethane and combined with the dichloromethane solution previously obtained. After washing with brine, drying (K_2CO_3), and concentration, there remained a light yellow solid which was filtered through 2 in. of silica gel with ethyl acetate–hexane (1:3). No further purification was attempted to avoid enantiomer enrichment. The naphthamide thus obtained was injected as a concentrated ethyl acetate solution onto a J. T. Baker Column (see General Methods section) with 5% isopropyl alcohol–hexane as the eluent at 3.0 mL/min. The separations were base line for the racemic naphthamides, prepared in the same way from *tert*-butyl formamidines,[4] and >98% ee for the product from **16a**, **16b** (Figure 1).

(10) Private communication from Dr. Arnold Brossi, National Institutes of Health. Dr. Brossi has prepared **9**, mp (oxalate salt, mp 183 °C) and performed elemental analysis which were in accordance with the calculated values.

(11) Schnider, O.; Brossi, A.; Vogler, K. *Helv. Chim. Acta* **1954**, *37*, 710.
(12) Schnider, O.; Grussner, A. *Helv. Chim. Acta* **1949**, *32*, 321.

(S)-N-Methyl-1-(p-methoxybenzyl)-1,2,3,4,5,6,7,8-octahydroisoquinoline (19a). A solution of 0.094 g (0.36 mmol) of the (S)-1-(p-methoxybenzyl)-1,2,3,4,5,6,7,8-octahydroisoquinoline (**16a**) in 2 mL of ethyl formate was heated at 40 °C for 15 h. The reaction mixture was concentrated in vacuo, and the crude formamide was dissolved in 5 mL of diethyl ether to which 0.035 g (0.92 mmol) of lithium aluminum hydride was added. After 2 h of stirring at room temperature, the reaction was quenched successively with 5 drops of water, 3 drops of 20% aqueous KOH solution, and 5 drops of water. The solution was filtered and concentrated, and the crude product was subjected to bulb-to-bulb distillation (0.05 mmHg; 110 °C), which afforded 0.088 g (89%) of the product as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.75 (1 OH, m), 2.36 (3 H, s), 2.50 (1 H, m), 2.77 (2 H, m), 2.90 (2 H, m), 3.77 (3 H, s), 6.80 (2 H, d, J = 8.7 Hz), 7.16 (2 H, d, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 22.9, 23.2, 28.1, 28.2, 30.1, 35.7, 42.8, 47.3, 55.0, 66.2, 113.2, 127.0, 129.1, 129.8, 132.9, 157.3; $[\alpha]^{24}_D$ -76.9° (c 2.9, ether), lit.[11] $[\alpha]^{25}_D$ -78.9° (c 3.0, ether).

Dextrorphan [(+)-3-Hydroxy-17-methylmorphinan] (4a). A solution of 0.139 g (0.51 mmol) of **19a** in 1 mL of phosphoric acid was heated[12] at 135-140 °C for 65 h under argon. The mixture was poured over ice and neutralized with concentrated ammonium hydroxide. Extraction with benzene-ether, drying (K_2CO_3), and concentration in vacuo gave a crude product which was purified via radial chromatography; silica gel, 1 mm thickness, eluted with hexane-triethylamine-ethyl acetate (60:15:25), to give 0.060 g (45%), mp 188-190 °C: $[\alpha]^{24}_D$ +54.0° (c 3.0, ethanol). An authentic sample[13] showed $[\alpha]_D$ +56.3° (c 3.0, ethanol), mp 191-193 °C.

(13) We thank Dr. John Scott, Hofmann-LaRoche for a sample. Previous preparation of (+)-**4a** has been described: Schnider, O.; Grussner, A. *Helv. Chim. Acta* **1951**, *34*, 2211.

(S)-1-Benzyl-1,2,3,4,5,6,7,8-octahydroisoquinoline (16b). In a manner analagous to the preparation of **16a**, **16b** was obtained in 82% yield and HPLC analysis of its naphthamide showed that the enantiomeric excess was 99 ± 1%. The product **16b** was obtained as an oil, via vulb-to-bulb distillation (135 °C, 0.05 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.7 (5 H, m), 1.9 (6 H, m), 2.8 (3 H, m), 3.2 (2 H, m), 7.3 (5 H, br s).

(S)-N-Methyl-1-benzyl-1,2,3,4,5,6,7,8-octahydroisoquinoline (19b). In a manner analogous to **19a**, **19b** was methylated in 82% yield to give an oil, purified by bulb-to-bulb distillation (135 °C, 0.05 mmHg): ^{1}H NMR ($CDCl_3$) δ 1.58 (4 H, m), 1.87 (6 H, m), 2.35 (3 H, s) 2.57 (1 H, t, J = 5 Hz), 2.84 (4 H, m), 7.23 (5 H, m); $[\alpha]^{24}_D$ +9.9° (c 2.87, ethanol).

Morphinan 4b. In a manner similar to the formation of **4a**, the octahydroisoquinoline **19b** was heated in phosphoric acid to give **4b** in 57% yield. The product was purified with radial chromatography using conditons identical with that employed for **4a**: ^{1}H NMR ($CDCl_3$) δ 1.34 (7 H, m), 1.70 (3 H, m), 2.05 (1 H, d of t, J = 2.5, 12.2 Hz), 2.39 (3 H, s), 2.40 (2 H, m), 2.63 1 H, dd, J = 5.6, 18.3 Hz), 2.80 (1 H, br m), 3.03 (1 H, d, J = 18.3 Hz), 7.15 (3 H, m), 7.24 (1 H, d, J = 7.6 Hz); $[\alpha]^{24}_D$ +56.9° (c 1.50, ethanol). reported for the (-)-antipode, $[\alpha]^{25}_D$ -56° (ethanol), mp 33-34 °C.[14] **4b** was obtained as an oil, which did not crystallize.

Acknowledgment. This study was supported by the National Science Foundation. A.I.M. thanks the Alexander von Humboldt Foundation for a Senior Scientist Award (1984-1986) and the Faculty at the University of Wurzburg for their hospitality.

(14) Henecka, H. *Liebigs Ann. Chem.* **1953**, *583*, 110.

Synthesis of Vinyl Selenides or Sulfides and Ketene Selenoacetals or Thioacetals by Nickel(II) Vinylation of Sodium Benzeneselenolate or Benzenethiolate

H. J. Cristau,* B. Chabaud,* R. Labaudiniere, and H. Christol

Laboratoire de Chimie Organique (U.A. 458), ENSCM, F-34075 Montpellier Cêdex, France

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The substitution of a bromine atom on a double bond by benzeneselenolate or benzenethiolate anions is catalyzed by the bis(bipyridine)nickel(II) bromide complex. Various alkenyl selenides or sulfides and seleno- or thioacetals are prepared in good to excellent yields.

A number of useful functional group transformations can be achieved with vinyl selenides or sulfides. Owing to their ability to stabilize carbanionic intermediates for further functionalization and/or the easy removal of the metalloid, they have been widely used in organic synthesis. As a matter of fact, their preparations have held attention these past years, and several methods have been proposed. The preparations of vinyl senelides generally imply multiple steps procedures involving addition of electrophilic selenium on triple or double bonds followed by elimination reactions[1] or Wittig-type reactions with α-selenated ylides.[1f,2] Other possible preparations are the reaction of phosphorus tetraiodide or triiodide with selenoacetals or seleno esters,[1f] the reduction of phenylselenoalkynes,[1d] the reaction of alkynyl trialkyl borates,[1e] alkenylboranes, and alkenyl mercurials,[1d] selenyl halides, or diaryl selenides, the addition of selenic acids[1f,3] and selenols[4] on alkynes, and the syn elimination of selenoacetals monoselenoxides.[5] Vinyl sulfides are obtained by Wittig reaction[6] or addition of a thiolate on a triple bond.[7] Ketene thioacetals are prepared by Wittig,[8] Wittig-Horner,[9] and Peterson[10] re-

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