Asymmetric Michael Reactions of 3,5-Dihydro-4*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepine with Methyl Crotonate

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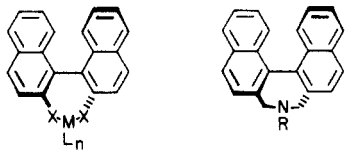
Received December 16, 1985

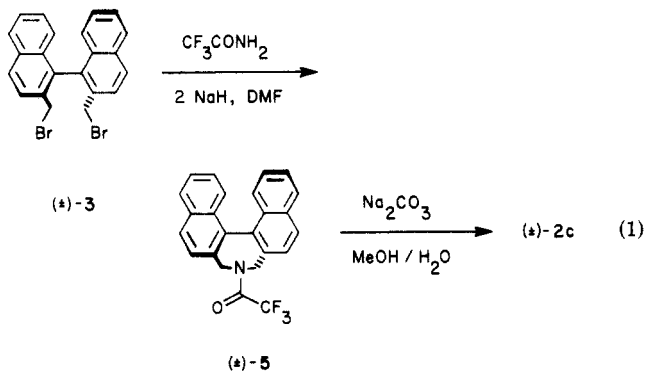
The rigid and symmetric 1,1′-binaphthyl moiety has found extensive use in chiral auxiliaries for asymmetric synthesis. Most commonly, chelates of structure **1** have been used, where the X's are donor sites and ML_n is the metallic site of reaction.[1] Alternatively, fixed rings such as dihydroazepines of structure **2** have been applied. The



1 **2a**, R = $CH_2^+{}_2$
2b, R = CLiPhCN
2c, R = H
2d, R = Li
2e, R = CHPhCONH$_2$

latter include Cram's chiral catalyst for the addition of alkyllithiums to aldehydes, **2a**,[2] and Mazaleyrat's chiral acyl anion equivalent for aldehyde additions, **2b**.[3] Continuing our interest in the development of C_2 symmetric chiral auxiliaries for metal-mediated asymmetric reactions,[4,5] we have studied diastereoselective Michael additions of 3,5-dihydro-4*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepine (**2c**) and its lithium amide **2d** with methyl crotonate.[6] We describe below our results with this asymmetric carbon–nitrogen bond-forming reaction.

Our synthesis of **2c** is shown in eq 1. Failing to effect direct reaction of ammonia with dibromide (±)-**3**, we used 2,2,2-trifluoroacetamide (**4**) as an ammonia synthon.[7] Treatment of (±)-**3**[8] with 1 equiv of **4** and 2 equiv of sodium hydride in dimethylformamide (DMF) at room temperature for 2.5 h gave amide (±)-**5** in 59% yield.[9] Hydrolysis of (±)-**5** with sodium carbonate in aqueous methanol (room temperature, 17 h)[10] then gave (±)-**2c** in 99% yield. Resolution of **2c** was accomplished by a single crystallization of the dibenzoyltartrate salt from methanol. The homochiral free base from the dibenzoyl-L-tartrate salt, (*S*)-**2c**,[11] 100% ee based on chiral stationary-phase HPLC analysis of the corresponding 1-naphthamide,[12] was then obtained in 45% (90% of theory) yield from the



(±)-**3** (±)-**5** (±)-**2c** (1)

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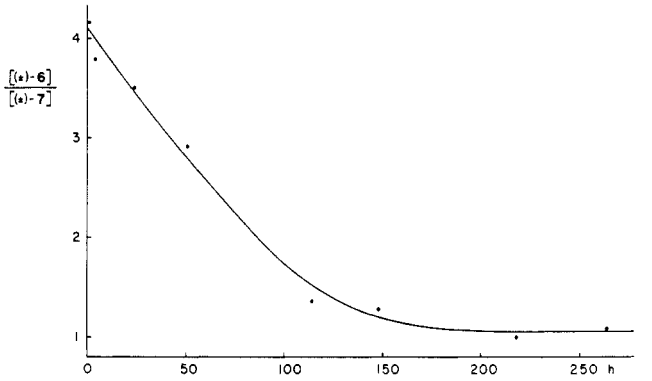
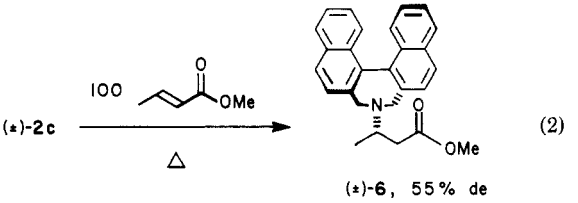


Figure 1. Diastereomer ratio vs. time during the thermal Michael addition (eq 2).

racemate.[13,14] Structurally, **2c** is distinguished from other C_2 symmetric chiral secondary amines[15–17] in that it has only two stereoisomers; i.e., there is no corresponding *meso* isomer which must be separated from the *d,l* isomers.

Diastereoselective Michael additions were first examined thermally with the free amine **2c**. Methyl crotonate was chosen as a model substrate in order to simplify NMR analysis. Treatment of (±)-**2c** with a large excess of methyl crotonate at reflux for 21 h yielded amino ester (±)-**6** as a 3.5:1 mixture of diastereomers in 68% yield (eq 2). The



(±)-**2c** (±)-**6**, 55% de (2)

diastereomer ratio was evident from both ^{1}H NMR and HPLC[18] analysis. The indicated isomer prevailed ac-

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(11) Absolute configuration assigned by optical rotation.[3]
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(13) Both enantiomers of dibenzoyltartaric acid monohydrate are commercially available (Aldrich) allowing isolation of (*R*)-**2c** from the free base of the mother liquor from the first crystallization.
(14) The overall yield of (*S*)-**2c** from (±)-**3** (26% = 53% of theory) compares favorably with the yields of Mazaleyrat's recently described syntheses of (*S*)-**2c** (21% = 41% of theory) and (*R*)-**2c** (15% = 30% of theory) from (±)-**3** via the diastereomers of **2e**.[3]
(15) Whitesell, J. K.; Felman, S. W. *J. Org. Chem.* **1977**, *42*, 1663.
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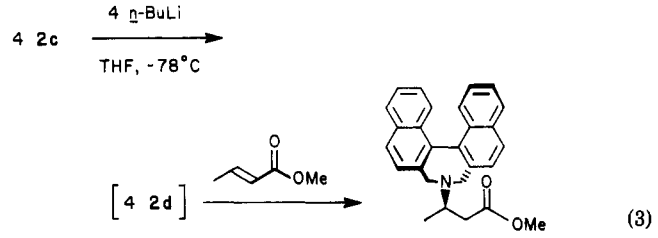
cording to the correlation discussed below. HPLC analysis of aliquots from an identical reaction showed that the ratio of diastereomers started at 4.1:1 and decreased until leveling off at 1.0:1 (Figure 1). This behavior is consistent with an initial kinetically controlled addition[19] (4.1:1), followed by equilibration to the thermodynamic product (1.0:1). Equilibration may have occurred by reversible addition[20] or by flipping of the binaphthyl configuration.[21]

Michael additions of the lithium amide **2d** occurred with greater diastereoselectivity than the free amine. Treatment of a tetrahydrofuran (THF) solution of 4 equiv of (±)-**2c** at ca. −78 °C with a precooled THF/hexane solution of 4 equiv of *n*-butyllithium generated a dark solution, which, after 25 min, was treated with a precooled THF solution of 1 equiv of methyl crotonate (eq 3). After 30



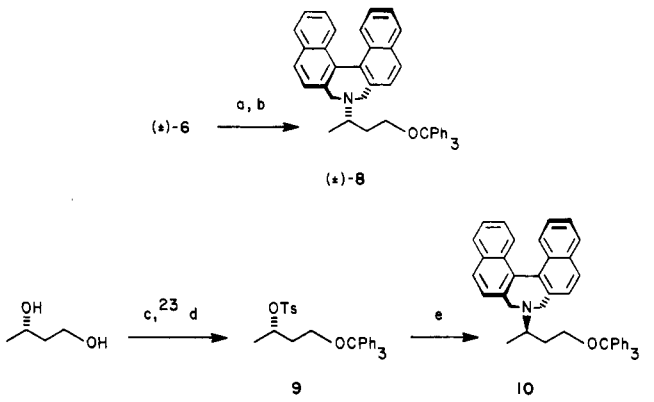
(3)

7, 98% de (racemic)
97% de (homochiral)

min at ca. −78 °C,[22] quenching and standard workup yielded the amino ester (±)-**7** as a *94:1* mixture of diastereomers in 88% yield. An excess of **2d** was required; use of 2 and 1 equiv reduced the yield to 41% and 15%, respectively. Similar treatment of (*S*)-**2c** gave **7** as a 61:1 mixture of diastereomers in 81% yield. High selectivity with both racemic and homochiral **2d** is consistent with primary control of the diastereoselectivity by the chirality of the incoming nucleophile as opposed to other more complicated scenarios involving aggregated molecules of lithium amide. The face selectivities of the thermal (4.1:1 favoring α-approach) and lithium amide (61–94:1 favoring β-approach) Michael additions correspond to diastereomeric transition state energy differences of 1.1 and 1.6–1.8 kcal/mol at their respective temperatures of 120 and −78 °C.

The relative stereochemistry in **6** and **7** was correlated by converting the thermal Michael adduct (±)-**6** (3.5:1) to amino ether (±)-**8** by standard chemistry and comparing it with **10**, prepared by coupling the homochiral fragments (*S*)-**9** and (*S*)-**2c** (Scheme I).[24,25] The minor diastereomer of (±)-**8** was found to correspond to **10** by ^{1}H NMR analysis.[26] The relative stereochemistry in the major diastereomer of **6** is therefore as shown.

Scheme I[a]



[a] (a) 2 equiv of $LiAlH_4$, THF, 0 °C, 30 min, 86%; (b) 6 equiv of $CClPh_3$, 55% DMAP, TEA/CH_2Cl_2, room temperature, 53 h, 74%; (c) 1.1 equiv of $CClPh_3$, 4% DMAP, TEA/CH_2Cl_2, room temperature, 13 h, 93%; (d) 2 equiv of TsCl, 5% DMAP, py, room temperature, 43 h, 75%; (e) 2 equiv of (*S*)-**2c**, DMF, 86 °C, 2 h, 45%.

Since the binaphthyl moiety is attached to adducts **6** and **7** by benzylic carbon–nitrogen bonds, it should be removable by reductive techniques.[8,27] Accordingly, diastereoselective addition of homochiral **2d** to a Michael acceptor, followed by reductive cleavage, should correspond to the enantioselective addition of an asymmetric ammonia synthon.

Experimental Section

All reactions were performed under a dry nitrogen atmosphere. Tetrahydrofuran was dried by distillation from the sodium benzophenone ketyl. Dichloromethane, dimethylformamide, and pyridine were dried over 3A molecular sieves. Methyl crotonate was distilled and dried over 4A molecular sieves. *n*-Butyllithium was titrated according to Ronald's procedure.[28] HPLC was detected at 280 nm. Elemental analyses were performed by Robertson Laboratory, Inc.

(±)-4-(2,2,2-Trifluoroacetyl)-3,5-dihydro-4*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepine (5). To a stirred room temperature suspension of 0.545 g (13.6 mmol) of a 60% oil dispersion of sodium hydride in 50 mL of dry dimethylformamide was added 0.770 g (6.82 mmol) of **4**, causing gentle foaming for ca. 1 min. After 15 min, 3.00 g (6.82 mmol) of (±)-**3** was added, causing vigorous gas evolution. Gas evolution gradually diminished over the next 10 min as the solution cleared and turned yellow-green. After being stirred 2.5 h at room temperature, the reaction mixture was treated with 50 mL of saturated NaCl (aqueous) and extracted with ether (2 × 50 mL). The combined ether extracts were washed with saturated NaCl (2 × 50 mL), dried (Na_2SO_4), and concentrated to give 2.98 g of yellow oil. Flash chromatography (8% ethyl acetate in hexane) yielded 1.57 g (59%) of white solid, which was used for further transformations: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.97 (t, J = 9.8 Hz, 4 H), 7.62–7.43 (m, 6 H), 7.33–7.24 (m, 2 H), 5.31 (d, J = 13.6 Hz, 1 H), 4.84 (d, J = 13.6 Hz, 1 H), 4.02 (d, J = 14.0 Hz, 1 H), 3.71 (d, J = 14.0 Hz, 1 H). A small sample was recrystallized from hexane: mp 163–165 °C; IR (mull) 1690, 1200, 1140, 825, 751 cm^{-1}. Anal. Calcd for $C_{24}H_{16}NOF_3$: C, 73.65; H, 4.12; N, 3.58; F, 14.56. Found: C, 73.91; H, 4.25; N, 3.37; F, 14.64.

(±)-3,5-Dihydro-4*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepine (2c). A solution of 0.873 g (2.23 mmol) of (±)-**5** in 60 mL of methanol was treated with a solution of 0.516 g (4.87 mmol) of Na_2CO_3 in 10 mL of water. The resulting colorless solution with white precipitate was stirred at room temperature for 17 h before the methanol was removed in vacuo, 50 mL of 5% NaOH (aqueous) was added, and the solution was extracted with ether (2 × 60 mL).

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The combined ether extracts were washed with 5% NaOH (3 × 40 mL), dried (Na_2SO_4), and concentrated to afford 0.650 g (99%) of white solidified foam: mp 147–149 °C; IR (mull) 3335, 1098, 820, 778, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 8.02–7.94 (m, 4 H), 7.58 (d, J = 8.3 Hz, 2 H), 7.50–7.43 (m, 4 H), 7.31–7.23 (m, 2 H), 3.85 (d, J = 11.7 Hz, 2 H), 3.53 (d, J = 11.7 Hz, 2 H), 2.12 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 134.80, 134.63, 132.84, 131.17, 128.69, 128.08, 127.12, 126.84, 125.55, 125.16, 48.40.

(*S*)-(+)-3,5-Dihydro-4*H*-dinaphth[2,1-*c*:1′,2′-*e*]azepine (2c). A solution of 2.09 g (7.09 mmol) of (±)-**2c** in 235 mL of methanol was added slowly with gentle mixing to a solution of 2.67 g (7.09 mmol) of (−)-dibenzoyl-L-tartaric acid monohydrate in 400 mL of methanol at room temperature. White needles began to form upon standing 1 h. After 24 h, the mixture was cooled to 0 °C for 30 h and then to −20 °C for 15 h. Filtration yielded 2.12 g of pale yellow needles: mp 170–175 °C (dec).

A 0.992 g sample of this material was slurried in 70 mL of ether and treated with 50 mL of 5% NaOH (aqueous) with stirring, giving two cloudy phases. The ether phase was separated, and the aqueous phase was extracted with ether (2 × 50 mL). The combined ether phases were washed with 5% NaOH (2 × 40 mL) and water (2 × 30 mL), dried (Na_2SO_4), and concentrated to give 0.444 g (45% = 90% of theory, based on (±)-**2c**) of white solidified foam: mp 73–84 °C; $[\alpha]^{20}_D$ +620° (*c* 0.78, $CHCl_3$) [lit.[3] $[\alpha]^{20}_D$ +574.8° (*c* 0.7, $CHCl_3$)]; IR (mull) 1090, 1030, 819, 770, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 7.99–7.94 (m, 4 H), 7.58 (d, J = 8.7 Hz, 2 H), 7.50–7.44 (m, 4 H), 7.30–7.24 (m, 2 H), 3.86 (d, J = 12.1 Hz, 2 H), 3.52 (d, J = 12.1 Hz, 2 H), 1.82 (br s, 1 H).

A small sample of free base was derivatized with 1-naphthoyl chloride (pyridine, ca. 95 °C, 45 min) and analyzed by chiral stationary-phase HPLC (Regis Pirkle Type 1-A, 25 cm × 4.6 mm i.d., two columns in series; 10% isopropyl alcohol in hexane, 2.6 mL/min, retention times of racemate: 27.6 and 33.0 min), indicating 100% ee favoring the first eluted enantiomer.

Thermal Michael Additions. A solution of 0.150 g (0.508 mmol) of (±)-**2c** in 5.4 mL (51 mmol) of dry methyl crotonate was heated at reflux for 21 h. The resulting clear orange solution was cooled and concentrated in vacuo (rotory evaporator followed by 0.5 mm overnight) to 0.199 g of brown oil. Flash chromatography (50% ethyl acetate in hexane) yielded 0.137 g (68%) of very pale yellow oil: IR (neat film) 1733, 1200, 1143, 819, 754, 735, 503 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.94 (dd, J = 4.0, 7.7 Hz, 4 H), 7.58 (d, J = 8.4 Hz, 2 H), 7.47–7.40 (m, 4 H), 7.27–7.22 (m, 2 H), 3.82–3.64 (m, 5 H), 3.52–3.32 (m, 3 H), 2.70–2.60 (m, 1 H), 2.40–2.29 (m, 1 H), 1.20 (d, J = 6.2 Hz, 1.0 H, diastereomeric methyl protons), 1.13 (d, J = 7.0 Hz, 2.0 H, diastereomeric methyl protons); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 172.80, 172.72, 134.79, 134.73, 134.27, 134.16, 132.95, 131.22, 128.55, 128.19, 127.87, 127.41, 125.65, 125.32, 56.86, 56.74, 56.56, 56.45, 51.94, 51.52, 40.38, 40.26, 18.30, 18.19; HPLC (Regis Pirkle Type 1-A, 25 cm × 10 mm i.d.; 5% isopropyl alcohol in hexane, 1 mL/min, retention times 41.13 and 44.02 min) 3.48:1, favoring the first eluted diastereomer.

Aliquots, 0.5 mL, were syringed from an identical reaction, rapidly cooled in an ice bath, passed through a plug of silica gel with 50% ethyl acetate in hexane, and analyzed by HPLC as above: diastereomer ratio (time); 4.16:1 (1 h), 3.79:1 (4 h), 3.50:1 (23 h), 2.91:1 (51 h), 1.36:1 (114 h), 1.28:1 (148 h), 1.00:1 (218 h), 1.09:1 (264 h).

Lithium Amide Michael Additions. To 5 mL of dry tetrahydrofuran in a −78 °C bath was added 0.219 mL (0.508 mmol) of *n*-butyllithium (2.32 M in hexane). The resulting solution was added dropwise via cannula over 3 min to a solution of 0.150 g (0.508 mmol) of (±)-**2c** in 5 mL of dry tetrahydrofuran rapidly stirred in a −78 °C bath. The resulting dark green solution was stirred 25 min at −78 °C before treatment with a solution of 13.5 μL (12.7 mg, 0.127 mmol) of dry methyl crotonate in 2.3 mL of dry tetrahydrofuran precooled in a −78 °C bath dropwise via cannula over 1.3 min. The resulting brown solution was stirred 30 min at −78 °C before quenching with a solution of 27.2 mg (0.508 mmol) of NH_4Cl in 7 mL of water and warming to room temperature. The majority of tetrahydrofuran was removed in vacuo before the solution was extracted with dichloromethane (2 × 30 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo (1 mm, overnight) to 0.169 g of orange oil. Flash chromatography (50% ethyl acetate in hexane) yielded 44.2 mg (88%) of yellow oil: ^1H NMR ($CDCl_3$, 250 MHz) δ 7.95–7.92 (m, 4 H), 7.58 (d, J = 8.3 Hz, 2 H), 7.47–7.40 (m, 4 H), 7.27–7.21 (m, 2 H), 3.80 (d, J = 12.3 Hz, 2 H), 3.66 (s, 3 H), 3.42 (d, J = 12.3 Hz, 2 H), 3.40–3.30 (m, 1 H) 2.66 (dd, J = 5.3, 14.4 Hz, 1 H), 2.37 (dd, J = 8.7, 14.4 Hz, 1 H), 1.20 (d, J = 6.6 Hz, 3 H); HPLC (as above) 94:1, favoring the second eluted diastereomer.

A similar procedure employing (*S*)-**2c** yielded 40.8 mg (81%) of clear oil: $[\alpha]^{25}_D$ +267° (*c* 2.46, $CHCl_3$); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.95–7.91 (m, 4 H), 7.58 (d, J = 8.4 Hz, 2 H), 7.48–7.40 (m, 4 H), 7.27–7.21 (m, 2 H), 3.79 (d, J = 12.3 Hz, 2 H), 3.66 (s, 3 H), 3.42 (d, J = 12.3 Hz, 2 H), 3.40–3.30 (m, 1 H), 2.65 (dd, J = 5.4, 14.5 Hz, 1 H), 2.37 (dd, J = 8.7, 14.5 Hz, 1 H), 1.20 (d, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 172.82, 134.85, 134.16, 132.99, 131.30, 128.60, 128.21, 127.86, 127.44, 125.69, 125.37, 56.55, 51.99, 51.58, 40.40, 18.31; HPLC (as above) 61:1, favoring the second eluted diastereomer.

Acknowledgment. We are grateful to Professor K. Barry Sharpless for providing laboratory facilities and financial support (NIH Grant GM-28384) for this independent project. J.M.H. thanks the Fannie and John Hertz Foundation for a graduate fellowship (1982–1986), and G.C.F. thanks the MIT Undergraduate Research Opportunities Program for partial support.

Registry No. (±)-**2c**, 102518-95-6; (*S*)-(+)-**2c**, 97551-09-2; (*S*)-**2c** (dibenzoyl L-tartrate salt), 102493-59-4; **3**, 64091-25-4; **5**, 102493-57-2; **6** (diastereomer 1), 102518-96-7; **6** (diastereomer 2), 102493-60-7; CF_3CONH_2, 354-38-1; $CH_3CH{=}CHCO_2CH_3$, 18707-60-3.

Regio- and Stereoselective Dehydrogenation of α,ω-Diols Catalyzed by a Rhodium Hydride Complex

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Received November 6, 1985

The hydrogen-transfer reaction from an alcohol to a hydrogen acceptor catalyzed by transition-metal complexes giving the oxidized product[1] has attracted much interest and now is recognized to be one of useful processes in organic synthesis. When a diol was used as the starting alcohol the corresponding lactones could be readily obtained.[2] Very recently we have found that certain ruthenium complexes are excellent catalysts for the stereo-[3] and regioselective[4] lactone formation reaction from substituted diols. It is of interest that for the lactone formation reaction from unsymmetrically substituted diols, the ruthenium-catalyzed system using an α,β-unsaturated ketone as a hydrogen acceptor exhibits a regioselectivity

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