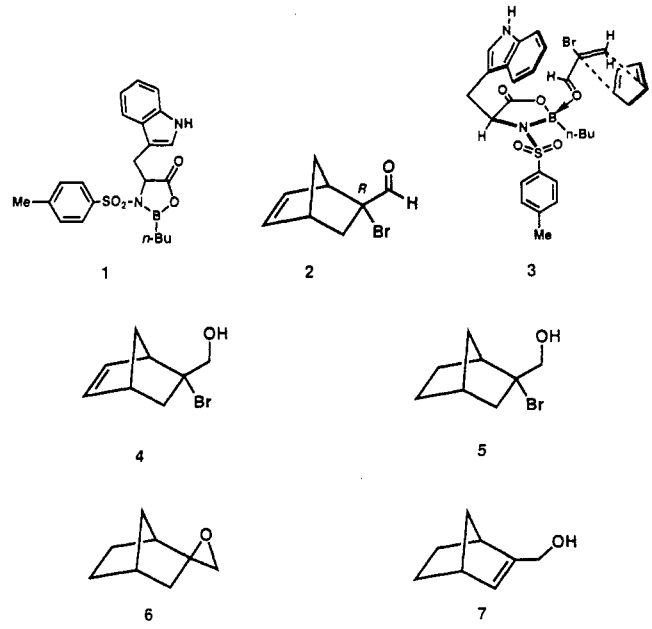
127.3, 128.5, 142.7, 167.7; MS m/z 340 (M^+), 163, 120, 105, 77.

Preparations and characterizations of ***N*-butylmethoxyphenylacetamide (2), *N*-(1-phenylethyl)-4-nitrobenzamide (4), *N*-(1-phenylethyl)acetamide (5),** and ***N*-(1-phenylethyl)-2,2-dimethylpropanamide (6)** are given in ref 3. **2-(2-Pyridyl)propanamide (3)** was provided by Dr. M. Zuanic, Chemica, Inc., Los Angeles, CA 90064.

***N*-(1,1-Dimethylethyl)methoxyphenylacetamide (7)**:[3] mp 94.6–95.4 °C; ^{1}H NMR 1.34 (s, 9 H), 2.16 (s, 3 H), 5.96 (s, 1 H), 7.3–7.4 (m, 5 H); ^{13}C NMR 20.9, 28.4, 51.4, 75.5, 128.5, 128.6, 128.7, 135.3, 167.2, 169.1; MS m/z 249 (M^+), 150, 149, 108, 107, 79, 57.

2,6-Bis[(2-phenylpropanoyl)amino]pyridine (8):[3] mp 186.4–187.8 °C; ^{1}H NMR 2.26 (s, 6 H), 6.20 (s, 2 H), 7.4–7.8 (m, 13 H), 8.45 (s, 2 H); ^{13}C NMR 21.0, 75.7, 110.3, 127.5, 128.9, 129.4, 134.6, 140.8, 148.7, 166.8, 169.9.

Acknowledgment. We are grateful to the Louisiana State Board of Regents for providing an Education Quality Support Fund grant (1990–91 ENH-53) that enabled the purchase of the NMR spectrometer used in this work.



A Simple Enantioselective Synthesis of (1*S*,4*R*)-Bicyclo[2.2.1]hept-2-ene-2-methanol

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The power of organic synthesis has been expanded in recent years by advances in catalytic enantioselective reactions mediated by chiral Lewis acids.[1-4] One of the most effective systems is the (*S*)-tryptophan-derived oxazaborolidine **1** which has been shown to be an outstanding catalyst for enantioselective Diels–Alder and Mukaiyama aldol-type reactions.[3,4] For example the Diels–Alder reaction of α-bromoacrolein and cyclopentadiene yields adduct **2** with >200:1 enantioselectivity via the transition-state assembly **3** in which the aldehyde and the Lewis acid form a charge-transfer complex.[3b] This note describes the application of this chemistry to the enantiospecific synthesis of the chiral allylic alcohol **7**,[5] in a formal sense of the Diels–Alder adduct of 2-(hydroxymethyl)cyclopentadiene and ethylene, a reaction for which there is currently no direct enantioselective version.

Reaction of **2** (prepared as described previously[3a]) with 1 molar equiv of sodium borohydride in wet tetrahydrofuran (THF) led to clean reduction of the aldehyde to yield bromo alcohol **4** in 95% yield after recrystallization.[3a,6] Reduction of the double bond was accomplished by hydrogenation, in the presence of palladium on carbon, in ethyl acetate (EtOAc) which afforded, after filtration through silica gel, alcohol **5** as a low-melting solid in 99% yield. The saturated bromo alcohol **5** was then converted to epoxide **6**, in 99% yield, by the action of excess sodium methoxide in methanol (MeOH).[7] Finally, base-catalyzed isomerization to the allylic alcohol **7** with 2 equiv of lithium diethylamide gave, after chromatography, (1*S*,4*R*)-bicyclo[2.2.1]hept-2-ene-2-methanol (**7**) in 93% yield and 87% overall yield from **2**.[8,9]

The versatility and usefulness of the catalyst **1** as an entry to optically pure 2-substituted norbornenes has been demonstrated through a concise and high-yielding conversion of **2** to allylic alcohol **7**. The allylic alcohol **7** and epoxide **6** both represent useful intermediates for further elaboration of these systems. The development of these intermediates into interesting chiral ligands will be the topic of future reports.

Experimental Section

General Methods. Nuclear magnetic resonance spectra were obtained in deuteriochloroform at the frequency indicated. Proton spectra are reported in ppm with chloroform (7.26 ppm) as internal reference. Carbon spectra were referenced to the deuteriochloroform triplet, center peak at 77 ppm. All solvents were distilled prior to use standard purification methods. Mass spectra were determined by the Harvard Chemistry Department Mass Spectrometry Facility.

(1*R*,4*R*,5*R*)-5-Bromobicyclo[2.2.1]hept-2-ene-5-methanol (4). To the aldehyde **2** (4.72 g, 23.4 mmol) in THF (20 mL) was added H_2O (0.5 mL) followed by $NaBH_4$ (0.90 g, 23.8 mmol). After 10 min of stirring the reaction mixture was poured into H_2O (30 mL), extracted with ether (4 × 50 mL), dried over $MgSO_4$, and concentrated to afford alcohol **4** quantitatively. The alcohol was further purified by recrystallization from hexane to afford **4** (4.48 g, 95%) as crystalline solid:[3a] mp 74–76 dec; $[\alpha]^{23}_D$ = +78° (c = 0.96, $CHCl_3$); IR (KBr) 3239, 3069, 2990, 1053, 709 cm^{-1}; ^{13}C NMR

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(100 MHz) δ 137.3, 136.8, 79.3, 72.4, 50.6, 46.5, 42.1, 40.3; ^{1}H NMR (400 MHz) δ 6.32 (dd, J = 5.6, 3.1, 1 H), 6.15 (dd, J = 5.6, 3.1, 1 H), 3.85 (d, J = 12.5, 1 H), 3.73 (d, J = 12.5, 1 H), 3.24 (br s, 1 H), 2.92 (br s, 1 H), 2.21 (br s, 1 H, hydroxyl), 1.92 (dd, J = 13.6, 3.5, 1 H), 1.72 (dd, J = 13.6, 3.4, 1 H), 1.55 (m, 1 H), 1.48 (d, J = 9.3, 1 H); EIMS m/z 202 (M^+); HREIMS (M^+) calcd for $C_8H_{11}BrO$ 201.9994, found 202.0000.

(1*S*,2*S*,4*R*)-2-Bromobicyclo[2.2.1]heptane-2-methanol (5). To olefin **4** (3.43 g, 15.6 mmol) in EtOAc (100 mL) was added 10% Pd/C (200 mg), and a hydrogen atmosphere was secured. After being stirred for 4 h, the reaction mixture was filtered through a bed of silica gel and concentrated to yield alcohol **5** as a white solid (3.41 g, 99%): mp 39–41 °C; $[\alpha]^{23}_D$ = +47° (c = 1.78, $CHCl_3$); IR (KBr) 3336, 2963, 1064 cm^{-1}; ^{13}C NMR (100 MHz) δ 82.5, 71.4, 45.8, 45.2, 36.7, 36.5, 28.7, 28.1; ^{1}H NMR (300 MHz) δ 3.56 (ab, J = 12.5, Δν = 8.6, 2 H), 2.58 (br s, 1 H), 2.33 (br s, 1 H), 2.17–2.03 (m, 2 H), 1.92–1.77 (m, 2 H), 1.66–1.62 (m, 2 H), 1.50–1.16 (m, 3 H); CIMS m/z 222 ($M^+ + NH_4$): HRCIMS ($M^+ + NH_4$) calcd for $C_8H_{17}BrNO$ 222.0494, found 222.0475.

(1*S*,2*S*,4*R*)-Spiro[bicyclo[2.2.1]heptane-2,2′-oxirane] (6).[7] The bromo alcohol **5** (2.98 g, 13.4 mmol) was dissolved in methanol (25 mL) and treated with CH_3ONa (3.62 g, 67.0 mmol). The suspension was stirred for 4 h and then quenched by the addition of saturated aqueous NH_4Cl (75 mL) and extracted with ether (3 × 50 mL). The combined organic extracts were washed with brine (4 × 25 mL), dried over $MgSO_4$, and concentrated to afford quantitatively the crude epoxide which purified by chromatography (6:1 pentane–ether) to yield the volatile epoxide **6** as colorless oil (1.65 g, 99%): $[\alpha]^{23}_D$ = +58° (c = 0.97, $CHCl_3$); IR (neat, NaCl) 2955, 2871, 1060 cm^{-1}; ^{13}C NMR (100 MHz) δ 66.6, 50.4, 43.0, 38.4, 37.5, 36.5, 27.8, 24.8; ^{1}H NMR (400 MHz) δ 2.77 (d, J = 4.7, 1 H), 2.73 (d, J = 4.7, 1 H), 2.37 (br s, 1 H), 1.74 (d, J = 2.1, 1 H), 1.74–1.47 (m, 5 H), 1.34–1.11 (m, 3 H); EIMS m/z 124 (M^+); HREIMS (M^+) calcd for $C_8H_{12}O$ 124.0888, found 124.0834.

(1*S*,4*R*)-Bicyclo[2.2.1]hept-2-ene-2-methanol (7).[9] To ether at 0 °C was added diethylamine (2.92 mL, 28.2 mmol) followed by n-BuLi (2.5 M in hexanes, 11.3 mL, 28.2 mmol). The reaction mixture was maintained at 0 °C for 15 min and then warmed to ambient temperature. After 30 min the epoxide **6** (1.40 g, 11.3 mmol) in ether (25 mL) was added and the reaction mixture was heated to reflux. After an additional 2 h the reaction mixture was cooled, poured into H_2O (50 mL), and extracted with ether (3 × 50 mL). The combined organic extracts were dried over $MgSO_4$, concentrated, and purified by chromatography (2:1 pentane–ether) to yield the volatile allylic alcohol **7** (1.30 g, 93%): $[\alpha]^{23}_D$ = +38° (c = 0.35, $CHCl_3$); IR (neat, NaCl) 3328, 2960, 2868, 1018 cm^{-1}; ^{13}C NMR (126 MHz) δ 149.1, 129.1, 60.9, 48.3, 42.6, 42.1, 26.2, 24.7; ^{1}H NMR (400 MHz) δ 5.80 (s, 1 H), 4.20 (ab, J = 14.1, Δν = 25.2, 2 H), 2.84 (m, 2 H), 1.70–1.61 (m, 2 H), 1.42–1.38 (m, 2 H), 1.13 (d, J = 8.1, 1 H), 1.06–0.97 (m, 2 H); EIMS m/z 124 (M^+); HREIMS (M^+) calcd for $C_8H_{12}O$ 124.0888, found 124.0880.

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Additions and Corrections

Vol. 56, 1991

Joseph Frey, David A. Nugiel, and Zvi Rappoport*. Two Dimers Derived from the 2,4,6-Tri-*tert*-butylphenyl Radical, Formed during Reactions of the Aryllithium or the Grignard Reagent with Carbonyl Compounds.

Page 469, column 1, last line should read **X-ray crystal structure analysis of 1–2**: space group $P\bar{1}$.

Vol. 57, 1992

Ming-tain Lai, Eugene Oh, Younan Shih, and Hung-wen Liu*. Synthesis of Enantiomerically Pure [(Methylenecyclopropyl)acetyl]-CoA: The Causative Agent of Jamaican Vomiting Sickness.

Page 2471. Since publication of our synthesis, another example has come to our attention: Kabat, M. M.; Wicha, J. *Tetrahedron Lett.* **1991**, *32*, 531–532.

Zhen Yang, Henry N. C. Wong,* Po Ming Hon, Hson Mou Chang, and Chi Ming Lee. A Novel Synthesis of the Dibenz[*b*,*f*]oxepin Ring System: 10,11-Dihydro-11-hydroxydibenz[*b*,*f*]oxepin-10(11*H*)-one.

Page 4034, column 2. Supplementary Material Available should read ^{1}H- and ^{13}C-NMR spectra of **3**, **6**, **7**, and **8** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Ernesto G. Occhiato, Antonio Guarna,* Alberto Brandi, Andrea Goti, and Francesco De Sarlo. N-Bridgehead Polycyclic Compounds by Sequential Rearrangement–Annulation of Isoxazoline-5-spirocyclopropanes. 6. A General Synthetic Method for 5,6-Dihydro-7(8*H*)- and 2,3,5,6-Tetrahydro-7(1*H*)-indolizinones.

Page 4206, Scheme I. In formulas **5a–e** and **5f–h**, R_3 and R_4 must be inverted.

Rui Tamura,* Ken-ichiro Watabe, Noboru Ono, and Yukio Yamamoto. Asymmetric Synthesis of 3-Substituted 2-*exo*-Methylenealkanones by Addition–Elimination Reaction Using a Chiral Leaving Group and Organometallic Nucleophiles.

Page 4898, Scheme I. The β-methyl in compound **16** should be drawn in the α position.

Jung Lee and James K. Coward*. Enzyme-Catalyzed Glycosylation of Peptides Using a Synthetic Lipid Disaccharide Substrate.

Supplementary Material. The chemical shift values given in Figure 1a,b are in error due to setting the solvent reference peak at δ 3.1 ppm rather than δ 3.3 ppm. Therefore, in each of the three spectra, the entire spectrum should be displaced 0.2 ppm downfield; e.g., in Figure 1a and b, the pair of quartets centered at δ 2.7 ppm should be at δ 2.9 ppm.