at room temperature for 3 h. After evaporation of the solvent, the residue was chromatographed (SiO_2, benzene) to give **1b** (R = phenyl; 210 mg, 98%), mp 114.5–116 °C (lit.[3b] mp 115–116 °C).

When the electrolysis solution was worked up without addition of **3** (R = phenyl), there was obtained *N*-bromosuccinimide (**4**; 71 mg, 80% based on NaBr), mp 176–178 °C (lit.[6] mp 178.5 °C).

Electrolysis of a Mixture of 2a and 3 (R = Cyclohexyl) in Acetonitrile–Water. A suspension of **2a** (650 mg, 4.4 mmol), **3** (R = cyclohexyl; 460 mg, 2.0 mmol), and NaBr (30 mg) in a mixed solvent of acetonitrile (5 mL) and water (20 mL) was electrolyzed at 3 V, 2.0–1.2 mA/cm^2, at 23–27 °C. After the passage of 6.26×10^{-3} faradays of electricity for 24 h, the mixture was filtered and the solids were washed twice with water and once with benzene and air-dried to give **2a** (562 mg, 86%). The filtrate and washing were combined and extracted with ether. The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed (SiO_2, benzene) to give **3** (14 mg) and **5**[7] (321 mg, 61%): IR (neat) 1450, 1317, 1123 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.5 (m, 20, CH_2), 2.65–3.10 (m, 1, CH), 3.10–3.72 (m, 1, CH).

Electrolytic Cross-Coupling Reaction of Morpholine with Diphenyl Disulfide (3, R = Phenyl). A mixture of **3** (R = phenyl; 437 mg, 2.0 mmol) and morpholine (400 mg, 4.6 mmol) in acetonitrile (20 mL) containing NaI (30 mg) and Et_4NClO_4 (100 mg) was electrolyzed at 3 V, 5–1.2 mA/cm^2, at 15–22 °C for 18 h. Evaporation of the solvent followed by column chromatography (SiO_2, benzene–AcOEt) gave 718 mg (92%) of sulfenamide **6**:[8] IR (neat) 3150 (HC=C), 1585 (C=C), 1256, 1112, 927 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.86–3.10 (m, 4, CH_2N), 3.58–3.85 (m, 4, CH_2O), 1.18–7.61 (m, 5, HC=C).

Registry No.—**5**, 4837-39-2; **6**, 42267-53-8; morpholine, 110-91-8; phthalimide, 85-41-6; succinimide, 123-56-8.

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Facile Syntheses of Optically Active Terpene Sulfonic Acids. Application to the Resolution of (±)-Phenylglycine

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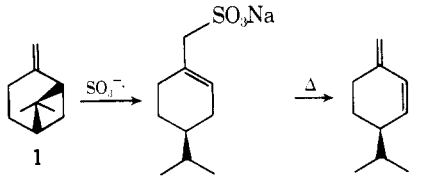
Received October 17, 1978

Although the resolution of racemic carboxylic acids by optically active amines is well documented, only two optically active sulfonic acids are available for the resolution of amines.[1] The availability of other optically active sulfonic acids, which could resolve amino acids, is desirable. The chirality of natural products such as terpenes makes these molecules suitable percursors for such synthesis. While the literature abounds with methods for the sulfonation of organic compounds[2] there exists a paucity of procedures for the simple preparation of optically active sulfonates, especially from olefins. Normal sulfonation reactions use SO_2, SO_3, $ClSO_3H$, oleum, etc., conditions which do not lend themselves readily to the preparation of sulfonates containing labile alternate functionalities. We wish to describe a new sulfonation reaction of β-pinene (**1**) as well as a remarkably facile synthesis of β-hydroxy sulfonates from optically active terpene epoxides.

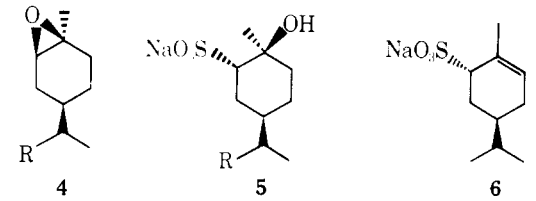
The radical addition of bisulfite at 110 °C and 45 psig to (−)-β-pinene (90.7% ee) (**1**) in the presence of an initiator and potassium nitrate[3] gave (−)-sodium (4*S*)-*p*-menth-1-ene-7-sulfonate (**2**) in ~50% yield. The ring opening of the bicyclic skeleton of β-pinene (**1**) is well known in attack by carbon



1 2 3

radicals;[4] however, sulfur-based radicals such as thiols and thioacetates yield shorter lived radical intermediates in which the integrity of the pinane structure is usually retained.[5] Acid ion-exchange chromatography gave the sulfonic acid of **2** as a brown syrup. The sulfonation of α-pinene[6] or camphene by this procedure proved less successful, the former undergoing competitive acid isomerization and hydration to α-terpineol and other products while the latter was recovered unchanged. The optical integrity of **2** was estimated by pyrolysis at 260 °C under reduced pressure, which gave (−)-β-phellandrene (**3**), $[\alpha]_d$ − 10.33°, as the major (90% GLC) menthadiene. This represents an optical purity of 65.0% for **3** or 71.6% retention of optical purity from **1**.[7] The partial racemization of **3** could arise by allylic hydrogen abstraction in **1** or **2** under free-radical conditions[8] or by a prototropic shift in **2** during pyrolysis. The formation of β-phellandrene (**3**) from **2** represents one of the few syntheses of optically active **3** in high chemical purity.[9] The cyclohexenylidene **3** is a product of kinetic control in the acid isomerization of *p*-menthadienes, from which it is usually obtained as a minor isomer.[10]

The preparation of a series of optically active β-hydroxy sulfonates was achieved by nucleophilic epoxide opening with sodium sulfite.[11] Thus (+)-*trans*-limonene oxide (**4a**) and (+)-*trans*-1,2-epoxy-*p*-menthane (**4b**, 97% ee) gave the hydroxy sulfonates (+)-(1*S*,2*S*,4*R*)-**5a** and (+)-(1*S*,2*S*,4*R*)-**5b**



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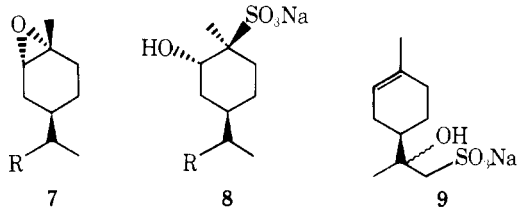

7 8 9

a, R = H_2C=
b, R = H_3C–

in 40.3 and 64% yield, respectively, after reflux with aqueous sodium sulfite. Analysis[12] of the white crystalline hydrates of **5a** and **5b** by NMR failed to show any evidence for products of reverse addition, unlike the nucleophilic addition of alkyl amines to these epoxides.[13] Similarly, (+)-*cis*-limonene oxide (**7a**) and (+)-*cis*-1,2-epoxy-*p*-menthane (**7b**) gave the hydroxy sulfonates (−)-(1*S*,2*S*,4*R*)-**8a** and (−)-(1*S*,2*S*,4*R*)-**8b** in 28 and 44.2% yield, respectively.[14] The (+)-limonene 8,9-epoxides

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yielded the tertiary hydroxy sulfonate (+)-(4*R*,8*RS*)-**9** as a mixture of diastereomers. Diimide reduction of **5a** and **8a** yielded **5b** and **8b**, while oxidation of **8b** gave a new β-keto sulfonate **10**. Consequently, it is possible to take advantage of the stereochemical control of trans diaxial epoxide opening to choose the formation of *p*-menthane secondary or tertiary hydroxy sulfonates. There appears to be no primary steric effect yielding mixed products from the *cis*-epoxide. The reactions take place in accordance with the predictions of the Furst–Plattner rule.[13] The formation of the corresponding diols[13] was the only side reaction from these epoxides.

Conversion of the salt **5b** to the corresponding acid was achieved by careful ion-exchange chromatography. Evaporation of the acid to dryness showed evidence of dehydration to (−)-(4*R*,6*S*)-**6**. Complete conversion to the unsaturated acid of **6** was achieved by refluxing an aqueous solution of **5b** containing acid ion-exchange resin. Severe rearrangement was observed on acidulation of the unsaturated hydroxy sulfonate **5a**. Acidification of the secondary hydroxy sulfonate **8b** gave the corresponding acid cleanly as a brown syrup, while **8a** showed evidence of rearrangement.

Analysis of the sodium sulfonate salts by ^{13}C NMR (see supplementary material) indicates that δ C–OH > C–SO_3Na. In **5a, 5b, 9, 11,** and **12** δ $C_6 > C_3 > C_5$ (e.g., 36.0, 28.0, and 25.3 respectively in **5a**), while in **10, 8a,** and **8b** δ $C_3 > C_6 > C_5$ (e.g., 43.5, 36.5, and 24.6, respectively, in **10**). ^1H NMR spectroscopy revealed that the hydroxy sulfonates **5** and **8** exist with the hydroxyl and sulfonate groups in the diequatorial conformation (C_2–H, dd, J_{aa} = 10–11.5 Hz, J_{ae} = 3–4 Hz) in contrast to the corresponding diaxial diols[16] (+)-*trans*-1-hydroxyneocarvomenthol (**11**) and (+)-*trans*-1-hydroxyneodihydrocarveol (**12**) (C_2–H, t, $J_{ae} \simeq J_{ee} \simeq$ 3–3.5 Hz). These conformational differences are reflected in the ^{13}C chemical shifts of the methyl and isopropyl groups and show excellent agreement with model compounds.[17]

The resolution of (±)-phenylglycine was carried out with the acid of **8b**, which gave the salt of L-(+)-phenylglycine as the less soluble diastereomeric salt in 97% optical purity.[18]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 137 spectrometer. All sulfonates exhibited the characteristic strong absorptions at 1150 and 1020 cm^{-1}. ^1H NMR spectra were measured using a 60-MHz Perkin-Elmer R-20B and ^{13}C NMR were measured at 60.905 MHz on a Supercon Hx-270 Fourier transform spectrometer in Me_2SO-d_6 solvent. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. Melting points are uncorrected. (±)-Phenylglycine (Aldrich) sublimed at 280–284 °C. Elemental analyses were carried out by Galbraith Laboratories Inc. Knoxville, Tenn.

(−)-Sodium (4*S*)-*p*-Menth-1-ene-7-sulfonate (2). (−)-β-Pinene (**1**), $[\alpha]_D$ −20.6° (neat, 90.7% ee) (1.21 mol), was heated at 110 °C in a 2-L Parr reactor with water (250 mL), sodium bisulfite (1.3 mol), potassium nitrate (0.13 mol), and oxygen (5 psig) for 4 h. A conventional initiator such as azobis(isobutyronitrile) may be used in place of oxygen. After cooling, the white hydrated sulfonate was collected by filtration and recrystallized from 90% ethanol, which yielded 148.3 g of monohydrate: $[\alpha]_D$ −64° (*c* 10.0, 1.0 N HCl); mp 200 °C up, slow dec; NMR δ 0.87 (d, *J* = 6 Hz, 6 H) 3.21 (s, 2 H, $-CH_2SO_3Na$), 5.48–5.7 (br s, H, CH=C). Anal. Calcd for monohydrate, $C_{10}H_{19}SO_4Na$: C, 46.49; H, 7.41; S, 12.41; Na, 8.90. Found: C, 46.46; H, 7.57; S, 12.53; Na, 8.70. *S*-(*p*-Chlorobenzyl)thiouronium salt mp 190 °C. Anal. Calcd for $C_{18}H_{27}O_3S_2N_2Cl$: C, 51.60; H, 6.45; S, 15.31; N, 6.69; Cl, 8.48. Found: C, 51.71; H, 6.54; S, 15.10; N, 6.66; Cl, 8.45.

(−)-β-Phellandrene (3). The sulfonate **2** (3 g) was heated in a round-bottom flask at 260 °C under vacuum (10 mm). The volatile products were distilled as they formed. GC/MS and IR showed the major product to be (−)-β-phellandrene (90%) with α-terpinene and α-phellandrene as the major impurities. Preparative GLC gave 97.8% of (−)-β-phellandrene.[7]

(+)-*cis*- and -*trans*-Limonene Oxides (7a and 4a). Conventional peracetic acid epoxidation of citrus (+)-limonene $[\alpha]_D$ 122.8° (neat, 97% ee) yielded **7a** and **4a**, which were separated by distillation in >99% purity on a 2 × 96 in. vacuum-jacketed column containing stainless steel protruded packing at a 59:1 reflux ratio.

(+)-*cis*-1,2-Epoxy-*p*-menthane (7b). Hydrogenation of *cis*-limonene oxide (**7a**), bp 74–75 °C (10 mm), $[\alpha]_D$ 43.7°, over platinum oxide without solvent in a Parr shaker at 50 psig yielded pure (+)-(1*R*,2*S*,4*R*)-1,2-epoxy-*p*-menthane (**7b**), $[\alpha]_D$ 48.2° (neat).

(+)-*trans*-1,2-Epoxy-*p*-menthane (4b). Similar hydrogenation of (+)-*trans*-limonene oxide, bp 76–77 °C (10 mm), $[\alpha]_D$ 89.8°, yielded pure (+)-(1*S*,2*R*,4*R*)-1,2-epoxy-*p*-menthane (**4b**), $[\alpha]_D$ 67.5° (neat).

General Conditions for Preparation of β-Hydroxy Sulfonates for Epoxides. A three-neck, 3-L Morton flask was charged with epoxide (0.86 mol), water (800 mL), and sodium sulfite (0.91 mol). The reaction was refluxed with high-speed mechanical stirring until the oil layer had disappeared. The crystalline hydrated hydroxy sulfonate precipitated on cooling. Filtration of the crystalline product was followed by ether washing the crystals to remove diol side products. Recrystallization from 90% ethanol yielded the pure crystalline hydrated β-hydroxy sulfonates. In the case of the *cis*-epoxides **7a** and **7b**, which were slower to react[14] than the *trans*-epoxides **4a** and **4b**, the inclusion of a phase-transfer agent and/or carrying out the reaction under pressure at 150 °C gave faster reaction.

(+)-Sodium (1*S*,2*S*,4*R*)-1-Hydroxy-*p*-menth-8-ene-2-sulfonate (5a): mp 238–240 °C; $[\alpha]_D$ 7.0° (*c* 20.06, H_2O); NMR δ 1.3 (s, 3 H), 1.7 (s, 3 H, $CH_3CH=$), 2.76 (dd, *J* = 4 and 10 Hz), 4.38 (br s, 2 H), 5.2 (s, H, OH). Anal. Calcd for dihydrate $C_{10}H_{21}SO_6Na$: C, 41.08; H, 7.24; S, 10.97; Na, 7.87. Found: C, 40.84; H, 7.33; S, 10.64; Na, 7.57.

(+)-Sodium (1*S*,2*S*,4*R*)-1-Hydroxy-*p*-menthane-2-sulfonate (5b): mp 195–200 °C; $[\alpha]_D$ 15.5° (*c* 10.0, H_2O); NMR δ 0.89 (d, *J* = 6 Hz, 6 H), 1.32 (s, 3 H), 2.66 (dd, *J* = 11 Hz, H), 5.24 (s, H, OH). Anal. Calcd for dihydrate $C_{10}H_{23}SO_6Na$: C, 40.80; H, 7.88; S, 10.89; Na, 7.81. Found: C, 40.70; H, 7.80; S, 11.00; Na, 7.56. (+)-Phenylglycine salt, mp 220–222 °C dec. Anal. Calcd for $C_{18}H_{29}NSO_6$: C, 55.79; H, 7.54; N, 3.62; S, 8.28. Found: C, 55.59; H, 7.70; N, 3.56; S, 8.06.

(−)-Sodium (1*S*,2*S*,4*R*)-2-Hydroxy-*p*-menth-8-ene-1-sulfonate (8a): mp 250–260 °C; $[\alpha]_D$ −2.69° (*c* 37.1, H_2O); NMR δ 1.18 (s, 3 H), 1.71 (s, 3 H, $CH_3C=$), 4.07 (complex doublet reduces to dd on D_2O exchange, H, *J* = 4 and 9.5 Hz), 4.6 (d, H, OH), 4.84 (br s, 2 H). Anal. Calcd for dihydrate $C_{10}H_{21}SO_6Na$: C, 41.08; H, 7.24; S, 10.97; Na, 7.87. Found: C, 40.94; H, 7.32; S, 11.22; Na, 7.61.

(−)-Sodium (1*S*,2*S*,4*R*)-2-Hydroxy-*p*-menthane-1-sulfonate (8b): mp 213–216 °C; $[\alpha]_D$ −5.2° (*c* 20.03, H_2O); NMR δ 0.8–1.0 (q, 6 H), 1.13 (s, 3 H), 4.5 (s, slightly split, H, OH). Anal. Calcd for dihydrate $C_{10}H_{23}SO_6Na$: C, 40.80; H, 7.88; S, 10.89; Na, 7.81. Found: C, 40.46; H, 7.97; S, 11.06; Na, 7.67.

Reduction of the Unsaturated Hydroxy Sulfonates 5a and 8a to 5b and 7b. The hydroxy sulfonates **5a** and **8a** (6 mmol) were separately dissolved in 90% ethanol. Hydrazine hydrate (98%, 40 mmol) was added to the solution at room temperature with stirring, followed by hydrogen peroxide (50%, 60 mmol) dropwise over 5 min. The reaction was stirred 2–20 h, followed by removal of the solvent at reduced pressure. Recrystallization of the white solid from 90% ethanol gave the saturated hydroxy sulfonates **5b** and **7b**, which were identified by IR and NMR.

Oxidation of 7b to Sodium (1*S*,4*R*)-2-Oxo-*p*-menthane-1-sulfonate (10). To the hydroxy sulfonate **7b** (0.39 mol) in water (50 mL) at 60 °C was added dropwise, with stirring, a solution of sodium dichromate (0.016 mol) and sulfuric acid (0.89 mol) in water (40 mL). The reaction was stirred a further 30 min after the addition was complete. Neutralization with sodium hydroxide followed by removal of water by rotary evaporation gave a yellowish solid which on recrystallization failed to give a crystalline product. Evaporation of the solvent gave a white solid **10**, which after drying in a vacuum oven was found to contain 4.6% water: mp 230–235 °C; NMR δ 0.85 (d, *J* = 6 Hz, 6 H), 1.18 (s, 3 H). Anal. Calcd for $C_{10}H_{17}SO_4Na(H_2O)_{0.7}$: C, 44.66; H, 6.90; S, 11.92. Found: C, 44.29; H, 6.96; S, 11.66.

(+)-Sodium (4*R*)-8-Hydroxy-*p*-menth-1-ene-9-sulfonate (9). Sulfonation of (+)-limonene 8,9-oxides,[19] $[\alpha]_D$ 97° (neat), yielded **9**: mp 205–215 °C dec; $[\alpha]_D$ 50° (*c* 4, H_2O); NMR δ 1.0 and 1.2 (s, 3 H, diastereomeric CH_3C), 1.62 (s, 3 H, $CH_3C=$), 2.71 (s, 2 H, $-CH_2SO_3Na$), 5.49 (d, H). Anal. Calcd for $C_{10}H_{17}SO_4Na$: C, 46.86, H, 6.69; S, 12.51, Na, 8.97. Found: C, 46.91; H, 6.81; S, 12.33; Na, 8.91.

(−)-Sodium (2*S*,4*R*)-*p*-Menth-6-ene-2-sulfonate (6). The hydroxy sulfonate **5b** (1.5 g) was refluxed in water (100 mL) containing Amberlyst-15 resin in the acid form (30 mequiv) for 7 h. Filtration of the resin followed by evaporation to dryness gave a brown oil identified by NMR as the unsaturated sulfonic acid of **6** (1.1 g, 99%). Basification followed by recrystallization gave the sodium salt **6**: mp 215–230 °C dec; $[\alpha]_D$ −185.7° (*c* 11.3, H_2O); NMR δ 0.87 (d, *J* = 6 Hz, 3 H), 0.84 (d, *J* = 6 Hz, 3 H), 1.85 (s, 3 H), 3.0 (d, *J* = 7 Hz, H), 5.5 (br

s, H). *S*-(*p*-Chlorobenzyl)thiouroium salt, mp 165–170 °C. (±)-Phenylglycine salt, mp 164–166 °C. Anal. Calcd for $C_{18}H_{27}NO_5S$: C, 58.51; H, 7.37; N, 3.79; S, 8.68. Found: C, 58.35; H, 7.51, N, 3.76; S, 8.44.

Resolution of (±)-Phenylglycine by Acid of 8b. The hydroxy sulfonate sodium salt **8b** (0.092 mol) in 90% ethanol was passed through an ion-exchange column in the acid form (ANGC-242). Evaporation of the solvent yielded the oily sulfonic acid, which was dissolved in water (90 mL), and to this was added (±)-phenylglycine (0.066 mol). The reaction mixture was heated and filtered and the filtrate was allowed to stand at room temperature overnight. Filtration gave 5.6 g of a crystalline adduct: mp 201–203 °C; $[\alpha]_D$ −48.2 ° (*c* 8.5, H_2O). Anal. Calcd for $C_{18}H_{29}NSO_6$: C, 55.79; H, 7.54; N, 3.62; S, 8.28. Found: C, 56.06; H, 7.49; N, 3.74; S, 8.03. To the adduct (2.0 g) in water (50 mL) was carefully added ammonium hydroxide to pH 8. Filtration of the resulting white plates gave (+)-phenylglycine (0.37 g): $[\alpha]_D$ +154° (1.0 N HCl) (lit.,[18] 158.6 ± 0.8°); sublimes 249–254 °C (lit.[18] 245–250 °C).

Acknowledgment. The authors are grateful to D. A. Johnson for the spectroscopic analyses and C. G. Cárdenas and P. A. Grieco for helpful discussions.

Registry No.—**1,** 19902-08-0; **2,** 69239-17-4; **2** *S*-(*p*-chlorobenzyl)thiouronium salt, 69239-19-6; **3,** 6153-17-9; **4a,** 6909-30-4; **4b,** 4680-25-5; **5a,** 69239-20-9; **5b,** 69239-21-0; **5b** (+)-phenylglycine salt, 69239-23-2; **6,** 69239-24-3; **6** *S*-(*p*-chlorobenzyl)thiouronium salt, 69307-88-6; **6** (±)-phenylglycine salt, 69307-89-7; **7a,** 4680-24-4; **7b,** 4959-34-6; **8a,** 69239-25-4; **8b,** 69239-26-5; **8b** free acid, 69239-27-6; **8b** (+)-phenylglycine salt, 69239-28-7; (4*R*,8*S*)-**9**, 69239-29-8; (4*R*,8*R*)**9,** 69239-30-1; **10,** 69239-31-2; **11,** 4031-57-6; **12,** 38630-75-0; (+)-limonene, 5989-27-5; (4*R*,8*R*)-limonene 8,9-oxide 28098-68-2; (4*R*,8*S*)-limonene 8,9-oxide, 28098-67-1; (±)-phenylglycine, 2835-06-5.

Supplementary Material Available: Complete ^{13}C NMR data for compounds, **2, 5, 6, 8, 9, 10, 11,** and **12** (1 page). Ordering information is given on any current masthead page.

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Synthesis and Stereochemistry of 2,6-Diphenyl-3-alkyltetrahydro-4-pyranones and the Corresponding 4-Pyranols

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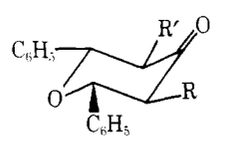
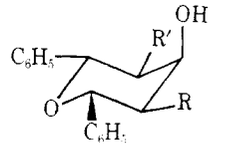
Received October 17, 1978

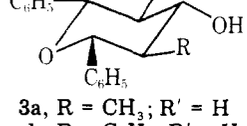
Japp and Maitland reported[1] the formation of a mixture of stereoisomeric diphenylmethyltetrahydro-4-pyranones during the condensation of benzaldehyde and 2-butanone in basic medium. However, in our hands such a condensation[2] afforded pure *r*-2,*cis*-6-diphenyl-*trans*-3-methyltetrahydro-4-pyranone (**1a**). Similarly, condensation of benzaldehyde with 2-pentanone yielded pure *r*-2,*cis*-6-diphenyl-*trans*-3-ethyltetrahydro-4-pyranone (**1b**). The structures of **1a** and **1b** were assigned primarily on the basis of ^1H NMR data. The relevant details are recorded in Table I. The ketones **1a–c** were



1a, R = CH_3; R′ = H
b, R = C_2H_5; R′ = H
c, R = R′ = CH_3



2a, R = CH_3; R′ = H
b, R = C_2H_5; R′ = H
c, R = R′ = CH_3



3a, R = CH_3; R′ = H
b, R = C_2H_5; R′ = H
c, R = R′ = CH_3

subjected to reduction with lithium aluminum hydride and with Meerwein–Ponndorf–Verley conditions. A mixture of epimeric alcohols resulted which was separated by column chromatography over alumina. The less strongly adsorbed axial alcohols were eluted in a petroleum ether–benzene mixture, and the more strongly adsorbed equatorial alcohols were eluted in benzene–ether fractions. The configuration and conformation of the pyranols were assigned on the basis of IR, ^1H NMR, and ^{13}C NMR spectral data, which are given in Tables II and III.

If a regular chair conformation is assumed for the heterocyclic ring, the two phenyl groups and the methyl group in **1a** or the ethyl group in **1b** may be expected to occupy the stable equatorial positions. Detailed information on the stereochemistry of 4-pyranones **1a** and **1b** can be gleaned from their ^1H NMR spectra. The signals at δ 4.33 (d, J = 11 Hz) and 4.81 (d, J = 10 and 5 Hz) for **1a** correspond to H(2) and H(6) protons, respectively. The observed large coupling constant

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