

removed by rotary evaporation to afford 0.622 g (4.45 mmol, 62%) of pure 1,2,2,4-tetramethyl-3-imidazolin-5-one as determined by  $^1\text{H}$  NMR spectroscopy. Vacuum distillation at 95–97 °C (18 torr) gave crystalline material with mp 42–44 °C. The pure imidazolinone had the following spectral properties: IR (KBr) 2.88, 3.37, 3.42, 5.88, 6.10  $\mu\text{m}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.43 (s, 6 H), 2.28 (s, 3 H), 3.01 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.6, 24.3, 25.5, 84.0, 162.8, 165.5; mass spectrum (70 eV),  $m/e$  (relative intensity) 140 (27.7), 125 (12.0), 83 (13.9), 82 (18.6), 71 (23.6), 56 (100), 43 (10.3), 42 (48.4); UV ( $\text{H}_2\text{O}$ ) 239 nm ( $\epsilon$  3570); ( $\text{CH}_2\text{Cl}_2$ ) 234 nm ( $\epsilon$  3380).

Anal. Calcd for  $\text{C}_7\text{H}_{12}\text{N}_2\text{O}$ : C, 59.98; H, 8.63; N, 19.98. Found: C, 60.03; H, 8.66; N, 19.94.

**1,2,5,6-Tetrahydro-1,3,5,5-tetramethyl-2-pyrazinone (6).** Sodium hydride (0.373 g as a 50% oil dispersion, 7.76 mmol) was added to 100 mL of tetrahydrofuran and the solution cooled to 0 °C. 1,2,5,6-Tetrahydro-3,5,5-trimethyl-2-pyrazinone (1.00 g, 7.14 mmol) as a saturated tetrahydrofuran solution was then added dropwise with a nitrogen atmosphere via a Hirschberg dropping funnel. Following a 10-min stirring period 0.55 mL (8.83 mmol) of methyl iodide in 10 mL of tetrahydrofuran was added. The reaction mixture was allowed to warm to ambient temperature with stirring overnight. The contents of the flask were transferred to a round-bottom flask, rinsing with methanol, and the solvents were removed by rotary evaporation. The product mixture was transferred to a separatory funnel with 20 mL of water and 15 mL of methylene chloride and extracted 10 times with 15 mL of methylene chloride. The combined methylene chloride extracts were then dried over sodium sulfate, and the methylene chloride was removed by rotary evaporation to yield 1.10 g (100%) of 1,2,5,6-tetrahydro-1,3,5,5-tetramethyl-2-pyrazinone (6). The pure pyrazinone had the following spectral properties: IR ( $\text{CHCl}_3$ ) 3.36, 3.39, 3.44, 3.52, 6.00, 6.13  $\mu\text{m}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.23 (s, 6 H), 2.14 (s, 3 H) 2.95 (s, 3 H), 3.20 (s, 2 H); mass spectrum,  $m/e$  (relative intensity) 154 (62), 111 (13), 82 (86), 56 (100), 42 (86), 41 (31); UV ( $\text{H}_2\text{O}$ ) 254 nm ( $\epsilon$  1768), 308 (sh, 200); ( $\text{CH}_2\text{Cl}_2$ ) 253 nm ( $\epsilon$  1490), 316 (sh, 110).

**1,4-Dimethyl-5-imidazolidinone (8).** A solution of 1.76 g (11.4 mmol) of 1,2,5,6-tetrahydro-1,3,5,5-tetramethyl-2-pyrazinone (6) in 140 mL of distilled, deionized water was irradiated with a 450-W Hanovia lamp in a Pyrex immersion well. The solution was continuously degassed with nitrogen, and progress of the reaction was monitored by analytical silica gel TLC, eluting with 10% methanol in methylene chloride (product,  $R_f$  0.29; starting material,  $R_f$  0.54) and visualizing with UV light and 10% phosphomolybdic acid in ethanol. After 96 h the reaction was complete. The solution was saturated with sodium chloride and continuously extracted with methylene chloride for 8 days. The methylene chloride extract was dried over sodium sulfate and the methylene chloride removed by rotary evaporation. The residue was 0.756 g (6.63 mmol, 58%) of 1,4-dimethyl-5-imidazolidinone (8), which was characterized from the following spectral data: IR ( $\text{CHCl}_3$ )

3.05, 3.36, 3.43, 3.51, 5.92  $\mu\text{m}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.33 (d,  $J$  = 7 Hz, 3 H), 2.87 (s, 3 H), 2.60 (br, 1 H), 3.53 (q,  $J$  = 7 Hz, 1 H), 4.33 (s, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) with off-resonance decoupling 16.2 (q), 26.9 (q), 54.3 (d), 63.8 (t), 174.9 (s); mass spectrum,  $m/e$  (relative intensity) 114 (41), 113 (11), 99 (12), 57 (88), 56 (34), 44 (100), 43 (20), 42 (44). The imidazolidinone 8 could not be sufficiently purified for combustion analysis because of instability.

**Irradiation of a Mixture of 1,2,5,6-Tetrahydro-3,5,5-trimethyl-2-pyrazinone (4) and 1,2,5,6-Tetrahydro-3,6,6-trimethyl-2-pyrazinone (5).** A solution of 0.77 g (5.55 mmol) of a 48:52 mixture of 4 and 5 in 50 mL of distilled, deionized water was irradiated with a 450-W Hanovia mercury lamp in a Pyrex immersion well. The reaction was continuously degassed with nitrogen and monitored by silica gel TLC, eluting with ethyl acetate (imidazolinone,  $R_f$  0.68; starting materials,  $R_f$  0.49; imidazolidinone,  $R_f$  0.12) and visualizing with UV light and a solution of 0.3% ninhydrin and 3% acetic acid in 1-butanol. After 97 h of irradiation the reaction was stopped even though some starting material was still present. The solution was saturated with sodium chloride and continuously extracted with methylene chloride for 94 h. The majority of the methylene chloride was rotary evaporated and the residue flash chromatographed through a 15 cm by 3 cm column of dry-packed 32–63- $\mu\text{m}$  silica gel. The column was eluted with 5% methanol in methylene chloride for the first 15 20-mL fractions and then with 20% methanol in methylene chloride for the next 12 20-mL fractions followed by 28% methanol in methylene chloride for the last 10 20-mL fractions. 1,2,2,4-Tetramethyl-3-imidazolin-5-one (7; 0.199 g, 1.42 mmol, 54% from pyrazinone 4) was obtained in fractions 7–10; starting pyrazinones (0.068 g, 0.48 mmol, 9%) in the ratio of 65:35 (4/5) as determined by  $^1\text{H}$  NMR spectroscopy was obtained in fractions 11–16; and 4-methylimidazolidinone (9; 0.072 g, 0.52 mmol, 25% from pyrazinone 5) was obtained in fractions 28–35. The imidazolidinone was characterized from the following spectral properties: IR ( $\text{CHCl}_3$ ) 3.00, 3.36, 3.43, 3.51, 5.91  $\mu\text{m}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.33 (d,  $J$  = 7.5 Hz, 3 H), 2.30 (br, 1 H), 3.48 (q,  $J$  = 7.5 Hz, 1 H), 4.40 (s, 2 H), 8.10 (br, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  180.2, 58.8, 54.4, 16.5; mass spectrum,  $m/e$  (relative intensity) 100 (30), 85 (39), 84 (12), 83 (70), 72 (14), 57 (78), 56 (28), 51 (25), 49 (100), 44 (45), 43 (14), 42 (16). The imidazolidinone 9 could not be sufficiently purified for combustion analysis because of instability.

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**Registry No.** 4, 82043-97-8; 5, 82043-98-9; 6, 82043-99-0; 7, 82044-00-6; 8, 82044-01-7; 9, 82044-02-8; 10, 82044-03-9; 11, 82044-04-0; 1,2-diamino-2-methylpropane, 811-93-8; ethyl pyruvate, 617-35-6.

## Synthesis with Hypochlorous Acid Functionalization of an Isopropenyl Group. Syntheses of (+)-Bilobanone and the Juvabiones

Shridhar G. Hegde and Joseph Wolinsky\*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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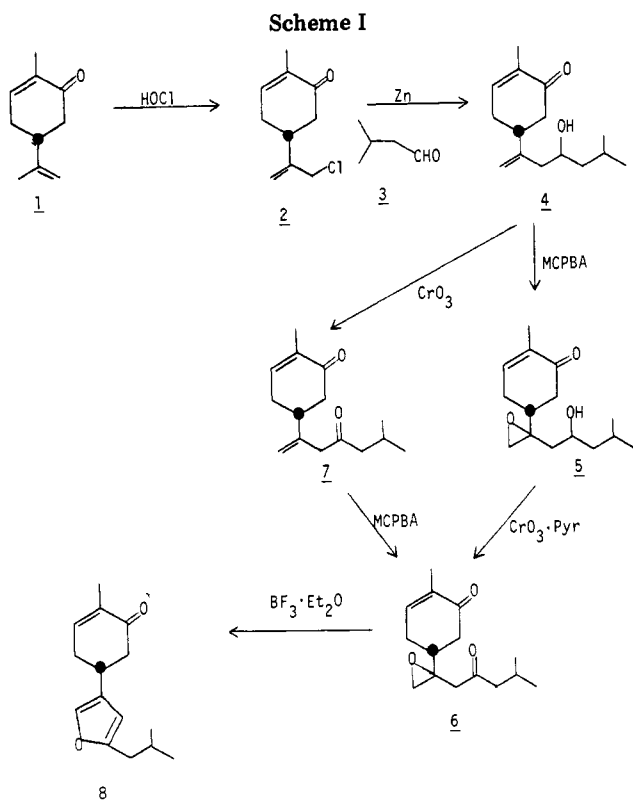
The two-phase reaction of HOCl with (+)-carvone and (+)-limonene monooxide affords 10-chlorocarvone (2) and 10-chlorolimonene monooxide (10), respectively. The organozinc reagents derived from these halides react with isovaleraldehyde to yield homoallylic alcohols with a bisabolane skeleton, which can be readily converted to (+)-bilobanone (8) and keto epoxide 13, which has previously been used as an intermediate in the synthesis of juvabione (14).

In a recent communication<sup>1</sup> we described the two-phase reaction of hypochlorous acid with certain olefins leading to the formation of allylic chlorides. We now demonstrate

that this reaction can be employed to functionalize an isopropenyl group in the presence of other reactive functional groups as illustrated in syntheses of (+)-bilobanone (8) and the juvabiones (14).

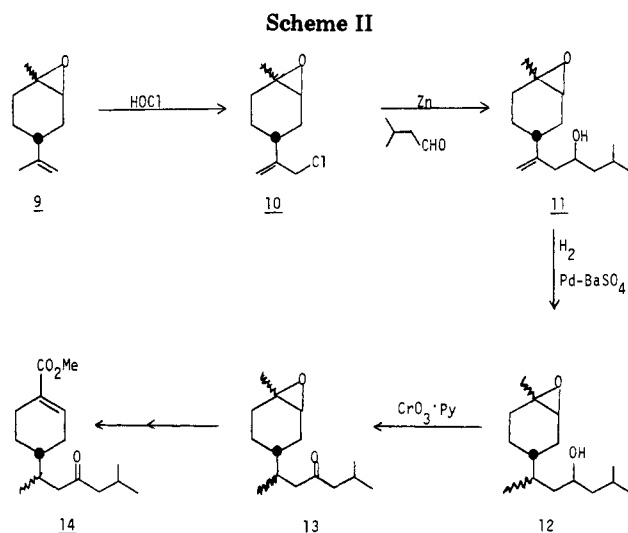
10-Chlorocarvone (2) is obtained in high yield by the reaction of HOCl with (+)-carvone (1).<sup>1</sup> Formation of an

(1) Hegde, S. G.; Vogel, M. K.; Saddler, J.; Hrinyo, T.; Rockwell, N.; Haynes, R.; Oliver, M.; Wolinsky, J. *Tetrahedron Lett.* 1980, 441.



organometallic from the allylic chloride in 2 followed by reaction with isovaleraldehyde (3) provides a convenient method for the construction of the bisabolane skeleton inherent in a wide variety of monocyclic sesquiterpenes.<sup>2</sup> Thus, treatment of chloride 2 with acid-washed zinc and isovaleraldehyde (3) in THF under reflux afforded the homoallylic alcohol 4 in 84% yield. The product appeared to be a mixture of stereoisomers; however, their separation was not attempted in view of the planned destruction of chirality at the alcohol carbon at a later stage in the synthesis.

Conversion of keto alcohol 4 to (+)-bilobanone, a furanosesquiterpene isolated from the heartwood of *Ginkgo biloba* L.<sup>3,4</sup> is outlined in Scheme I. Epoxidation of 4 with *m*-chloroperbenzoic acid in dichloromethane proceeded smoothly to yield epoxy keto alcohol 5 in high yield. Oxidation of 5 to the epoxy diketone 6 without destroying the epoxide moiety was achieved by a modified Collins procedure employing the chromium trioxide-pyridine complex in dichloromethane. Alternatively, 4 was first oxidized to the diketone 7, which was subsequently converted to epoxy diketone 6. The acid-catalyzed rearrangement of epoxy ketones derived from  $\beta,\gamma$ -unsaturated ketones has been utilized in the preparation of furans,<sup>5</sup> and in this instance it was observed that epoxy diketone 6 was almost quantitatively converted to bilobanone (8) by treatment with boron trifluoride etherate in a mixture of ether and THF. Bilobanone obtained by this route showed an optical rotation of  $+40^\circ$ , in good agreement with the value of  $+42^\circ$  reported for the natural product.<sup>4a</sup> The isomerization of epoxy diketone 6 can also be achieved by



warming with a catalytic amount of *p*-toluenesulfonic acid for a few minutes; however, in this instance the bilobanone showed an optical rotation of only  $+10^\circ$ , indicating extensive racemization had taken place.

We turn next to a description of a convenient route to *erythro*- and *threo*-juvabiones (14) as illustrated in Scheme II. Limonene monooxide (9) reacts cleanly with HOCl to afford 10-chlorolimonene monooxide (10).<sup>1</sup> Subsequent reaction of 10 with zinc and isovaleraldehyde (3) affords the homoallylic alcohol 11. Catalytic hydrogenation of 11 over Pd-BaSO<sub>4</sub> by employing ethyl acetate as solvent gave epoxy alcohol 12 in quantitative yield. Examination of molecular models of 11 suggests that hydrogen addition should occur with equal likelihood from both sides of the carbon-carbon double bond, leading to a mixture of *threo* and *erythro* isomers at the newly formed C-CH<sub>3</sub> center.

Oxidation of epoxy alcohol 12 with the chromium trioxide-pyridine complex in dichloromethane yields a mixture of epoxy ketone stereoisomers 13, whose spectra compare favorably with data reported in the literature.<sup>6</sup> The preparation of this mixture of 13 constitutes a formal total synthesis of *erythro*- and *threo*-juvabiones<sup>7,8</sup> since a procedure for the conversion of 13 to juvabione (14) has been described.<sup>6</sup>

### Experimental Section

All boiling points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Infracord. NMR spectra were determined with a Varian A-60A or a Perkin-Elmer R-32 spectrometer in CDCl<sub>3</sub> with tetramethylsilane as an internal standard. Mass spectra were recorded on a CEC-21-110-B high-resolution mass spectrometer. Microanalyses were performed by Dr. C. S. Yeh and associates.

**Preparation of 10-Chlorocarvone (2).** To a suspension of 10.3 g of "70%" calcium hypochlorite in 20 mL of water was added 11.65 g (77.7 mmol) of (+)-carvone (1) in 200 mL of dichloromethane. Approximately 60 g of dry ice was added in small portions to this mixture with stirring over a period of 2 h. At the end of this period, the reaction mixture was filtered to remove

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insoluble salts. The organic layer was separated, dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure. Distillation of the residue afforded 10.46 g (72%) of 2 as a colorless liquid: bp 107 °C (0.7 mmHg); IR 1681, 901, 749  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  236 nm ( $\epsilon$  4.1); NMR ( $\text{CDCl}_3$ )  $\delta$  1.75 (s, 3,  $\text{C}=\text{C}(\text{CH}_3)-\text{C}=\text{O}$ ), 2.1–3.0 (m, 5), 4.07 (s, 2,  $\text{CH}_2\text{Cl}$ ), 5.05, 5.24 (s, 2,  $=\text{CH}_2$ ), 6.75 (m, 1,  $\text{HC}=\text{C}-\text{C}=\text{O}$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_{13}\text{ClO}$ : C, 65.22; H, 7.07; Cl, 19.02. Found: C, 65.18; H, 7.33; Cl, 19.29.

**Preparation of 5-(4-Hydroxy-6-methyl-1-hepten-2-yl)-2-methyl-2-cyclohexenone (4).** A mixture of 3.67 g (20 mmol) of 10-chlorocarvone (2), 2.58 g (30 mmol) of isovaleraldehyde (3), 5.0 g of acid-washed zinc, and 25 mL of THF was refluxed under a nitrogen atmosphere for 8 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was diluted with water and extracted with ether. After washing with dilute HCl, saturated  $\text{NaHCO}_3$ , and saturated brine, the ether layer was dried ( $\text{MgSO}_4$ ) and concentrated under reduced pressure. Distillation of the residue yielded 3.97 g (84%) of 4 as a pale yellow liquid: bp 153 °C (1.0 mm);  $[\alpha]_D^{20} +60^\circ$ ; IR 3450, 1667, 1613, 1053, 909  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  0.9 (d, 6,  $J = 7.5$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.75 (s, 3,  $\text{H}_3\text{C}-\text{C}=\text{C}$ ), 3.65–3.75 (m, 1,  $\text{CHOH}$ ), 4.9 (s, 2,  $=\text{CH}_2$ ), 6.75 (b, 1,  $\text{H}-\text{C}=\text{C}-\text{C}=\text{O}$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{24}\text{O}_2$ : C, 76.27; H, 10.17. Found: C, 76.08; H, 10.21.

**Epoxydation of 4.** To a solution of 4.221 g (17.9 mmol) of the homoallylic alcohol 4 in 20 mL of dichloromethane was added 3.86 g (17.9 mmol) of 80% MCPBA in 120 mL of dichloromethane dropwise with stirring at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred for an additional 10 h at room temperature, washed with saturated  $\text{NaHCO}_3$ , saturated  $\text{Na}_2\text{S}_2\text{O}_3$ , and water, dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure. Distillation of the residue gave 3.47 g (77%) of the epoxy alcohol 5 as a pale yellow liquid: bp 151 °C (0.35 mmHg); IR 3448, 1667, 1613, 1053, 833  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  0.9 (d, 6,  $J = 8$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.7 (s, 3,  $\text{CH}_3-\text{C}=\text{C}$ ), 2.7–2.9 (m, 2,  $\text{H}_2\text{C}-\text{C}-\text{O}$ ), 3.5–3.9 (m, 1,  $\text{CHOH}$ ) and 6.78 ppm (m, 1,  $\text{H}-\text{C}=\text{C}-\text{C}=\text{O}$ ). Anal. Calcd for  $\text{C}_{15}\text{H}_{24}\text{O}_3$ : C, 71.43; H, 9.52. Found: C, 71.69; H, 9.58.

**Preparation of Epoxy Ketone 6.** Oxidation of 2.08 g (8.2 mmol) of the epoxy alcohol 5 using the  $\text{CrO}_3$ -pyridine complex according to the procedure of Ratcliffe and Rodehorst<sup>9</sup> yielded the crude epoxy ketone 6 in almost quantitative yield; IR 1709, 1667, 1613, 800  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ ) 0.9 (d, 6,  $J = 7.5$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.75 (s, 3,  $\text{H}_3\text{C}-\text{C}=\text{C}$ ), 2.6–2.9 (m, 2,  $\text{H}_2\text{C}-\text{C}-\text{O}$ ), 6.78 (m, 1,  $\text{HC}=\text{C}-\text{C}=\text{O}$ ); mass spectrum,  $m/e$  (rel intensity) 232 (57), 189 (56), 175 (30), 167 (39), 150 (54), 149 (47), 148 (60), 147 (50), 135 (46), 121 (46), 109 (50), 108 (45), 107 (53), 91 (51), 85 (74), 82 (55), 81 (48), 80 (40), 69 (46), 65 (30), 57 (100), 55 (58), 54 (56), 53 (59), 51 (33), 43 (60), 42 (25), 41 (65), 39 (56).

**Preparation of 5-(4-Keto-6-methyl-1-hepten-2-yl)-2-methyl-2-cyclohexenone (7).** To a solution of 3.29 g (13.9 mmol) of the keto alcohol 4 in 20 mL of acetone was added Jones reagent (prepared by dissolving 9.8 g of chromium trioxide in 7 mL of water followed by the addition of 0.87 mL of concentrated  $\text{H}_2\text{SO}_4$ ) dropwise with stirring at ambient temperature. The usual workup followed by distillation afforded 2.93 g (90%) of the diketone 7 as a pale yellow liquid: bp 128 °C (0.5 mmHg); IR 1724, 1681, 909  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ ) 0.85 (d, 6,  $J = 7.5$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.75 (s, 3,  $\text{H}_3\text{C}-\text{C}=\text{C}$ ), 3.15 (s, 2,  $=\text{C}-\text{CH}_2-\text{C}=\text{O}$ ), 4.95, 5.03 (two s, 1 each,  $=\text{CH}_2$ ), 5.7 (br, 1,  $\text{HC}=\text{C}-\text{C}=\text{O}$ ); mass spectrum,  $m/e$  (rel intensity) 234 (1.7), 150 (36), 149 (25), 135 (22), 109 (11), 91 (14), 85 (56), 82 (16), 79 (13), 77 (11), 57 (100), 55 (10), 54 (15), 53 (15), 43 (28), 41 (64), 39 (35).

**Epoxydation of the Diketone 7.** To a magnetically stirred solution of 2.1 g (9 mmol) of 7 in 15 mL of dichloromethane was added 1.83 g (9 mmol) of 85% MCPBA in 125 mL of dichloromethane dropwise at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred for an additional 24 h at ambient temperature, washed with saturated  $\text{NaHCO}_3$ , saturated  $\text{Na}_2\text{S}_2\text{O}_3$ , and saturated brine, dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure to obtain 1.87 g (83%) of the epoxy ketone 6.

**Acid-Catalyzed Rearrangement of 6.** To a magnetically stirred solution of 0.66 g (2.64 mmol) of epoxy ketone 6 in 5 mL

of ether-THF (1:1) was added 0.07 g (0.5 mmol) of  $\text{BF}_3$ -etherate under a nitrogen atmosphere. The reaction mixture was stirred at ambient temperature for 4 h, diluted with 20 mL of water, and extracted with ether. The ether extract was washed with saturated  $\text{NaHCO}_3$  and saturated brine, dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure. Distillation of the residue employing a microdistillation apparatus yielded 0.332 g of bilobanone (8) as a pale yellow liquid:  $[\alpha]_D^{20} +40^\circ$  (ethanol); IR 1667, 1639, 1550  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ ) 0.95 (d, 6,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.75 (br s, 3,  $\text{H}_3\text{C}-\text{C}=\text{C}$ ), 2.8–3.2 (m, 8), 5.9 (s, 1,  $\text{H}-\text{C}=\text{C}-\text{O}$ ), 6.7 (m, 1,  $\text{HC}=\text{C}-\text{C}=\text{O}$ ), and 7.1 (s, 1,  $\text{C}=\text{CH}-\text{O}$ ), which is in agreement with the data reported in the literature.<sup>4a,10</sup>

Alternatively, a mixture of 0.375 g (1.5 mmol) of epoxy ketone 6 and 0.05 g of *p*-toluenesulfonic acid was warmed to 70 °C for 10–15 min. After being cooled to room temperature and neutralization with saturated  $\text{NaHCO}_3$ , the reaction mixture was extracted with ether. The ether extract was washed with brine, dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure to obtain 0.213 g of the crude product, which contained mainly bilobanone (8) as determined by TLC (ether-pentane) and NMR. A microdistilled sample showed a specific rotation of  $+10^\circ$ .

**Preparation of 10-Chlorolimonenone Monoxide (10).** To a suspension of 6.7 g of “70%” calcium hypochlorite in 10 mL of water was added 7.6 g (50 mmol) of limonenone monoxide (9) in 200 mL of dichloromethane. Approximately 45 g of dry ice was added in small portions to this mixture with stirring over a period of 2 h. At the end of this period, the reaction mixture was filtered to remove insoluble salts. The organic layer was separated, dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure. Distillation of the residue afforded 7.02 g (75.5%) of 10 as a colorless liquid: bp 58–69 °C (0.3 mmHg); IR 1653, 909, 840, 752  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ ) 1.3 (two s, total 3 H,  $\text{CH}_3-\text{C}-\text{C}-\text{O}$  from two isomers), 1.4–2.2 (m, 7 H), 3.0 (m, 1 H,  $\text{H}-\text{C}-\text{C}-\text{O}$ ), 4.0 (s, 2H,  $\text{CH}_2\text{Cl}$ ), 4.95, 5.1, 5.2 (three s, total 2 H,  $\text{CH}_2=\text{C}$  from two isomers). Anal. Calcd for  $\text{C}_{10}\text{H}_{15}\text{ClO}$ : C, 64.52; H, 8.06; Cl, 18.82. Found: C, 64.38; H, 8.32; Cl, 19.00.

**Preparation of 2-[1-Methyl-7-oxabicyclo[4.1.0]-4-heptanyl]-6-methyl-1-hepten-4-ol (11).** A mixture of 4.2918 g (22.7 mmol) of 10-chlorolimonenone monoxide 10, isovaleraldehyde (2.0 g, 23.8 mmol), acid-washed zinc (8.4 g), and 20 mL of THF was refluxed under a nitrogen atmosphere for 10 h. Workup as described earlier and distillation gave 3.82 g (70.7%) of 11 as a colorless liquid: bp 120–130 °C (0.6 mmHg); IR 3448, 1640, 1053, 893, 840, 758  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ ) 0.9 (d, 6,  $J = 7.5$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.3 (s, 3,  $\text{CH}_3-\text{C}-\text{C}-\text{O}$ ), 3.0 (dd, 1,  $\text{H}-\text{C}-\text{C}-\text{O}$ ), 3.75 (seven-line pattern, 1,  $J = 5$  Hz,  $\text{CHOH}$ ), 4.85 (s, 2  $=\text{CH}_2$ ). Anal. Calcd for  $\text{C}_{15}\text{H}_{26}\text{O}_2$ : C, 75.63; H, 10.92. Found: C, 75.42; H, 11.17.

**Hydrogenation of the Epoxy Alcohol 11.** A solution of 11 (1.038 g, 4.36 mmol) in 15 mL of ethyl acetate was hydrogenated in a Brown hydrogenation apparatus using 0.095 g of 5% Pd-BaSO<sub>4</sub> catalyst. The solution was filtered through a plug of Celite, dried ( $\text{MgSO}_4$ ), and concentrated under pressure to afford 1.04 g of the crude epoxy alcohol 12: IR 3448, 1053, 847  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ ) 0.85–1.0 (br, 6 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.3 (s, 3,  $\text{H}_3\text{C}-\text{C}-\text{C}-\text{O}$ ), 2.9, and 3.0 (br, total 1 H,  $\text{H}-\text{C}-\text{C}-\text{O}$ ), 3.5–3.9 (m, 1 H,  $\text{CHOH}$ ).

**Preparation of the Epoxy Ketone 13.** Oxidation of the epoxy alcohol 12 (0.552 g, 2.3 mmol) using the  $\text{CrO}_3$ -pyridine complex according to the procedure of Ratcliffe and Rodehorst<sup>9</sup> yielded 0.448 g of the epoxy ketone 13. A microdistilled sample had the following spectral properties: IR 1724, 820  $\text{cm}^{-1}$ ; NMR ( $\text{CDCl}_3$ ) 0.8–0.95 (br, 6 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.3 (s, 3,  $\text{H}_3\text{C}-\text{C}-\text{C}-\text{O}$ ), 3.0 (br, 1 H  $\text{H}-\text{C}-\text{C}-\text{O}$ ), which is in good agreement with the data reported by Pawson and co-workers.<sup>8</sup>

**Registry No.** (+)-1, 2244-16-8; 2, 82044-96-0; 3, 590-86-3; 4 (isomer 1), 82044-97-1; 4 (isomer 2), 82044-98-2; 5, 82044-99-3; 6, 82045-00-9; 7, 82045-01-0; (+)-8, 17015-33-7; 9, 1195-92-2; 10, 74514-30-0; 11, 82045-02-1; 12, 82045-03-2; 13, 26666-83-1; 14 (isomer 1), 82079-49-0; 14 (isomer 2), 82079-50-3; calcium hypochlorite, 7778-54-3.

(9) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* 1970, 35, 4000.

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