

OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) in the ratio of 4:1 as judged by the relative intensities of the signals in the NMR (CHCl<sub>3</sub>) for the vinyl methyl group and the vinyl proton. **13**,  $\delta$  1.87 (d,  $J \approx 2$  Hz) and 5.92 (broad s); **14**,  $\delta$  2.03 (d,  $J \approx 2$  Hz) and 6.45 (broad s); for the mixture, IR (CHCl<sub>3</sub>) 1750 cm<sup>-1</sup>; NMR (CHCl<sub>3</sub>)  $\delta$  3.82 (s), 7.8–7.4 (m); mass spectrum,  $m/e$  (rel intensity) 282 (M<sup>+</sup>, 100), 254 (60), 226 (70), 198 (35), and 194 (40).

**Bicyclo[3.2.1]octenyl  $\gamma$ -Lactone 14.** Keto ester **11a** (110 mg, 0.39 mmol), prepared from keto acid **10a** by treatment with diazomethane (100% yield), and poly(phosphoric acid) (12 mL) were stirred for 2 h at 80 °C. The cooled mixture was poured into ice water and extracted with ether. The combined organic phases were washed with aqueous NaHCO<sub>3</sub>, dried, and then evaporated to give a residue which was crystallized from ether to yield 98 mg (82%) of pure lactone **14** (Ar = C<sub>6</sub>H<sub>5</sub>): mp 115–116.5 °C; IR (CHCl<sub>3</sub>) 1740 and 1645 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>)  $\delta$  1.60–2.40 (m, 6), 2.00 (d, 3,  $J = 1.5$  Hz), 2.80 (m, 1), 6.45 (b, 1), and 7.25–7.75 (m, 5); UV (MeOH) max 308 nm ( $\epsilon = 18$  000); mass spectrum,  $m/e$  (rel intensity) 252 (106), 224 (58), 196 (70), and 195 (50).

Anal. (C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>); Calcd mol wt, 252.1150. Found: 252.1153.

Under the conditions described above, both keto acid **10b** and keto ester **11b** furnished  $\gamma$ -lactone **14** (Ar = *m*-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) in yields of 92 and 88%, respectively; the crude product showed IR (CHCl<sub>3</sub>) 1745 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>)  $\delta$  2.0 (d, 3,  $J \approx 2$  Hz), 3.82 (s, 3), 6.45 (m, 1), and 7.8–7.5 (m, 4); UV (CH<sub>3</sub>OH) max 300 nm.

**Registry No.**—**3**, 4722-70-7; **5**, 67316-12-5; **6a**, 69089-24-3; **6b**, 69089-25-4; **7**, 69089-26-5; **9a**, 69102-09-6; **9b**, 69089-27-6; **10a**, 67315-97-3; **10b**, 67315-98-4; **11a**, 69089-28-7; **11b**, 69089-29-8; **13** (Ar = C<sub>6</sub>H<sub>5</sub>), 69089-30-1; **13** (Ar = *m*-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 69089-31-2; **14** (Ar = C<sub>6</sub>H<sub>5</sub>), 69089-32-3; **13** (Ar = *m*-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 69089-33-4; 2-cyclohexenone, 930-68-7; diethyl cyclohexanone-3-malonate ketal, 7084-90-4; ethyl cyclohexanone-3-acetate ketal, 7076-69-9; diethyl cyclohexanone-3-malonate, 22274-75-5.

### References and Notes

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### X-ray Structure of the $\gamma$ -Lactone Formed by Acid Treatment of Dihydroisopimaric Acid<sup>1</sup>

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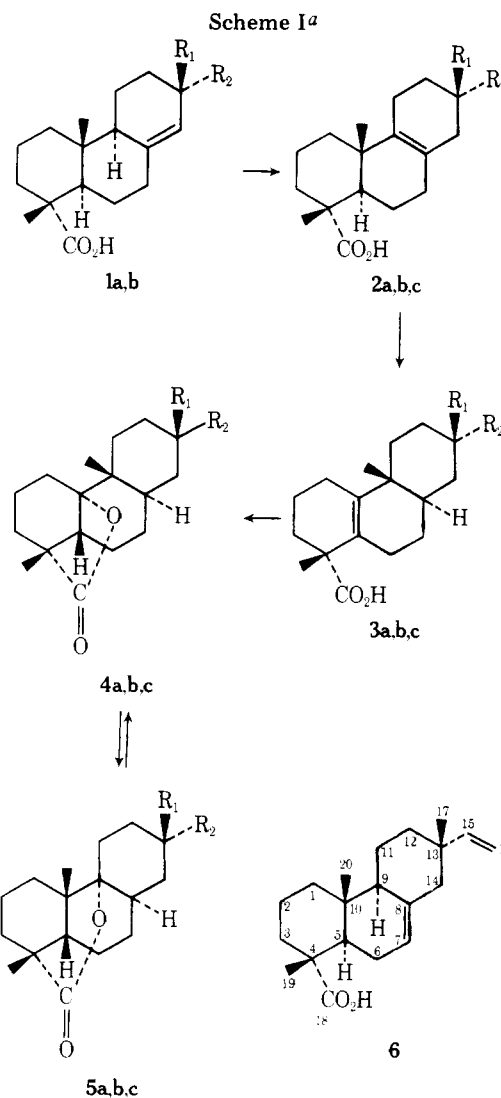
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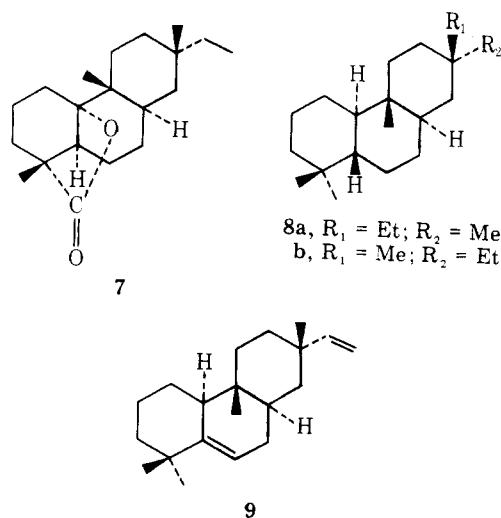
Exposure of various dihydroabiatic and dihydroleopimaric acids such as **1a** or **2a** to sulfuric acid at low temperature results in formation of a  $\gamma$ -lactone which under somewhat more stringent conditions is in equilibrium with a  $\delta$ -lactone.<sup>2</sup> The reaction has been formulated in terms of the backbone rearrangement shown in Scheme I, the stereochemistry assigned



<sup>a</sup> a series, R<sub>1</sub> = isopropyl, R<sub>2</sub> = H; b series, R<sub>1</sub> = Et, R<sub>2</sub> = Me; c series, R<sub>1</sub> = Me, R<sub>2</sub> = Et.

to **4a** and **5a** being based on mechanistic grounds.<sup>3-6</sup> The postulated stereochemistry of **4a** at C-8 and the intermediacy of compounds of type **3** have been verified,<sup>7</sup> but the presumed stereochemistries of **4a** and **5a** at C-5, while extremely plausible, have not been documented independently.

Dihydroisopimaric acid (**6**), dihydroisopimaric acid (**6**), and their double-bond isomers likewise undergo rearrangement to  $\gamma$ - and  $\delta$ -lactones which by analogy have been assigned



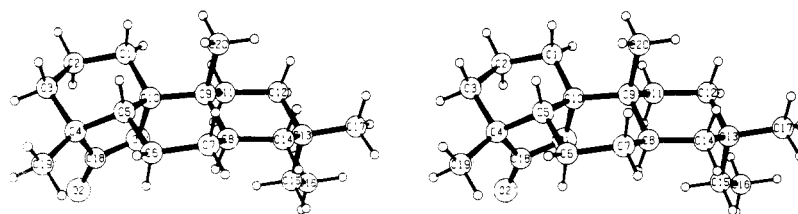


Figure 1. Stereoscopic view of **4c**.

formulas **4b**, **4c** and **5b**, **5c**, respectively.<sup>8-10</sup> Our subsequent preparation<sup>11</sup> of (-)-13-epirimuane (**8a**) from **4b** and of (-)-rimuane (**8b**) from **4c** by a method which leaves C-5 untouched confirmed the C-8 stereochemistry attributed to **4b** and **4c**, but did not furnish independent proof for the stereochemistry assigned to C-5 since the mode of hydrogenation of (-)-rimuene (**9**), which also furnishes **8b**, is difficult to predict.<sup>12</sup> Nevertheless, it has been generally accepted that H-5 is  $\beta$ .

In a recent publication, ApSimon and co-workers<sup>14</sup> claim that <sup>13</sup>C NMR shift data and spin lattice relaxation time measurements require revision of the previously accepted formula **4c** for the  $\gamma$ -lactone from dihydroisopimaric acid (**6**) to **7** with a cis-A/B ring junction, but agree with structure **5c** for the corresponding  $\delta$ -lactone. Presumably, their conclusions also apply to the  $\gamma$ - and  $\delta$ -lactones from **2a** and **2b**.<sup>15</sup> It is difficult to imagine how the equilibrium between  $\gamma$ - and  $\delta$ -lactones can involve epimerization at C-4 if compounds of type **3** can serve as precursors of the  $\gamma$ -lactones.

In view of the mechanistic problem and our interest in cationic rearrangements of diterpenes, we decided to settle the stereochemistry of the  $\gamma$ -lactones once and for all by X-ray crystallography. Our results on the  $\gamma$ -lactone from dihydroisopimaric acid show, contrary to the conclusions reached by the Canadian workers,<sup>14</sup> that this substance possesses structure **4c**, in accordance with the arguments used originally<sup>3,4</sup> to rationalize the rearrangement of **1a**. We infer that the  $\gamma$ -lactones from **2a** and **2b** also possess a trans-A/B ring junction. As a corollary, the hydrogenation of (-)-rimuene results in what appears to be addition of hydrogen from the more hindered  $\beta$  face.<sup>12</sup>

Crystal data for **4c** are listed in the Experimental Section. The crystal contained two independent molecules, in one of which (unprimed), due to thermal motion or disorder, C-16 was not well defined. Figure 1 is a stereoscopic drawing of the second (primed) molecule, which shows that the A/B ring junction is trans, with H-5  $\beta$  and H-8  $\alpha$ . Tables I and II, containing final atomic and anisotropic thermal parameters, and Tables III, IV, and V, listing bond lengths, bond angles, and selected torsion angles, are available as supplementary material. Since the crystal contained two independent molecules of **4c**, the tables of distances and angles contain two values for each entry.

### Experimental Section

Dihydroisopimaric acid was lactonized<sup>16</sup> by a slight modification of the literature method<sup>9</sup> by keeping it with sulfuric acid at  $-8^\circ\text{C}$  for 45 min and quenching with water. Extraction with ether, chromatography over silica gel, and elution with benzene gave **4c**, mp  $107.5$ – $108^\circ\text{C}$ , after recrystallization from aqueous methanol. Slow recrystallization from methanol furnished single crystals which were monoclinic, space group  $P2_1$ , with  $a = 11.775$  (1)  $\text{\AA}$ ,  $b = 12.450$  (1)  $\text{\AA}$ ,  $c = 12.859$  (2)  $\text{\AA}$ ,  $\beta = 104.68$  (1) $^\circ$ , and  $d_{\text{calcd}} = 1.109$   $\text{g cm}^{-3}$  for  $Z = 4$  ( $\text{C}_{20}\text{H}_{32}\text{O}_2$ ,  $M_r$  304.47). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu  $K\alpha$  radiation,  $\theta$ - $2\theta$  scans, pulse height discrimination). A crystal measuring approximately  $0.15 \times 0.25 \times 0.45$  mm was used for data collection; the data were not corrected for absorption ( $\mu = 5.4$   $\text{cm}^{-1}$ ). Of the 3851 accessible reflections for  $\theta < 76^\circ$ , 2763 were considered to be observed [ $I > 2.5\sigma(I)$ ]. The structure was solved by a multiple solution procedure<sup>17</sup> and was refined by block-diagonal least squares in which the matrix was par-

itioned into two blocks. In the final refinement, anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. Eleven low  $\theta$  reflections were strongly affected by extinction and were not included in the refinement. The final discrepancy indices are  $R = 0.051$  and  $wR = 0.052$  for the remaining 2752 observed reflections. The final difference map has no peaks greater than  $\pm 0.2$   $e \text{\AA}^{-3}$ .

Registry No.—**4c**, 59751-40-5; **6**, 5835-26-7.

**Supplementary Material Available:** Tables I–V listing final atomic and anisotropic thermal parameters, bond lengths, bond angles, and selected torsion angles (7 pages). Ordering information is given on any current masthead page.

### References and Notes

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### Methyl Effect in Electrophilic Additions. An Open Carbonium Ion Like Rate-Determining Transition State for the Bromination of Styrene

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Whereas bromination of aliphatic alkenes goes through bromonium ions,<sup>1</sup> open carbonium ion like transition states