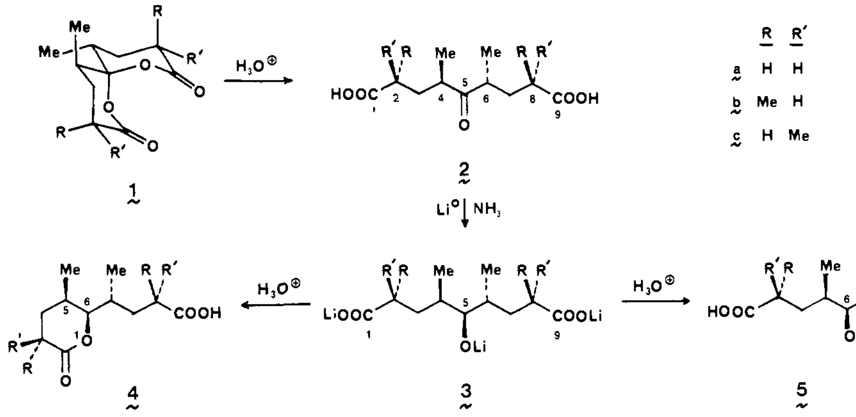
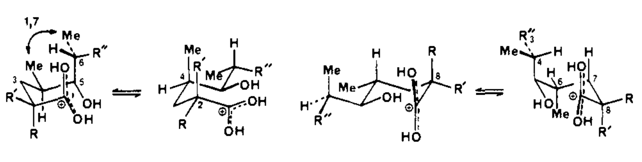
Scheme I



	R	R'
a	H	H
b	Me	H
c	H	Me

(4),H(7); H(6),H(3); C(5)-OH,H_{Me}; and $H_{Me(6)}$,R'] and one 1,6-H,O interaction [H(4),O(9)$_{ax}$] is unlikely to be involved. Since **7a** is destabilized by one additional gauche (1,6) interaction ($H_{Me(4)}$,R') relative to **8a** (i.e., ΔG° ≈ 0.9 kcal/mole), the observed 4.6:1 kinetic ratio of **5a**:**4a** is reasonable is one assumes that $\Delta G^{\ddagger}$ for the closure of each of **6a**–**9a** is identical. Ground-state conformational arguments would then, of course, translate directly into transition-state energy differences.

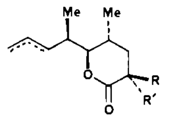

6 7 8 9

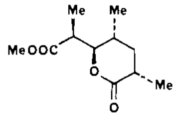
	R	R'	R''
a	H	H	CH$_2$CH$_2$COOH
b	Me	H	CH$_2$CH(Me)COOH
c	H	Me	"

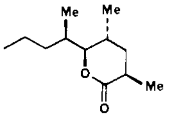
For **3b** (→**5b**:**4b** in 1.2:1) there is an identical number of 1,6-interactions in both **7b** and **8b**. Equal population of these preclosure conformations leads to the near unity kinetic ratio.

For **3c** (→**5c**:**4c** in ≥350:1[9]) there is no viable preclosure conformation that leads to the cis lactone (i.e., both **6c** and **7c** embody 1,7-interactions), and virtually all reaction proceeds via **8c**.

The stereochemical assignments for **1**–**5** were initially based upon extensive analysis of ^{1}H NMR data and the X-ray structure of dilactone **1b**.[2] Synthetic correlation to known compounds now supplements that evidence. Thus, oxidative decarboxylation (1.3 equiv of Pb(OAc)$_4$, 0.2 equiv Cu(OAc)$_2$·H$_2$O, 1.3 equiv of py, PhH, Δ)[10] of **5c** generated a mixture of olefins **10c** (~1:1), which was cleaved (NaIO$_4$, RuCl$_3$·3H$_2$O) to provide a pair of acids from which the methyl ester of Prelog–Djerassi lactone **11**[11] could be separated (32%) after diazomethane treatment. The Kochi reaction[10] of **5b** led to isomers **10b**, which were reduced (H$_2$, Pd/C) to *d,l*-invictolide (**12**, 59% from **5b**; 47% from **1b**), the recently isolated[12] queen recognition pheromone of the red imported fire ant. Each of these syntheses confirms the *trans*-5,6-disubstituted valerolactone nature of **5** and constitutes a highly stereoselective four-step preparation from **1b** or **1c**, themselves readily accessible in four pots from 3-pentanone and methyl acrylate.[2]


10b R=Me, R'=H
10c R=H, R'=Me


11


12

Acknowledgment. This investigation was supported by Grant 29077, awarded by the National Institute of General Medical Sciences, DHHS. Purchase of the Nicolet NT-300 WB NMR instrument was made possible through Grant NSF CHE 79-26027. We thank Drs. J. H. Tumlinson and J. R. Rocca for providing copies of high-field ^{1}H NMR spectra of invictolide.

---

(9) The observed "kinetic" ratio is critically dependent upon the precise conditions (pH and length of exposure to acid) for the quench of salt **3c**. The highest observed ratio was 350:1 (pH 3, rapid handling), but typical workup (pH ~2, 5 min for extraction) gave ratios in the still synthetically useful range of 20–150:1. Rapid, partial equilibration presumably accounts for this variability.

(10) Sheldon, R. A.; Kochi, J. K. "Organic Reactions"; Wiley: New York, 1972; Vol. 19, Chapter 4.

(11) Ireland, R. E.; Daub, J. P. *J. Org. Chem.* **1981**, *46*, 479.

(12) Rocca, J. R.; Tumlinson, J. H.; Glancey, B. M.; Lofgren, C. S. *Tetrahedron Lett.* **1983**, *24*, 1893.

Additions and Corrections

The Mechanism of the Dismutation of Superoxide Catalyzed by Copper(II) Phenanthroline Complex and of the Oxidation of Copper(I) Phenanthroline Complex by Oxygen in Aqueous Solution [*J. Am. Chem. Soc.* **1983**, *105*, 7276]. SARA GOLDSTEIN and GIDON CZAPSKI*

$E°_{O_2/O_2^-} = -0.33$ V which was used is defined for 1 at of O$_2$. In our calculations the value should be $E°_{O_2/O_2^-} = -0.16$ V which is defined for 1 M of O$_2$.

On page 7279 in the paragraph **Redox Potential of (op)$_2$Cu^{2+}** the following corrections should be made: $E°_{O_2/O_2^-}$ should be –0.16 V rather than –0.33 V; $E°_{(op)_2Cu^{2+}/(op)_2Cu^+}$ should be 0.11 V rather than –0.055 V; K_{12} should be 1.66×10^{13} rather than 5.62×10^{15}; and k_{-12} should be 1.77×10^{-5} M^{-1} s^{-1} rather than 5.25×10^{-8} M^{-1} s^{-1}.

On page 7280, 9th line in Conclusion: $E°_{(op)_2Cu^{2+}/(op)_2Cu^+}$ should be 0.11 V rather than –0.055 V.