Of particular interest is the interaction of dioxygen with some manganese derivatives. When O_2 is bubbled through an anhydrous toluene solution of yellow $[SiW_{11}Mn^{II}O_{39}]^{6-}$ (IV) it is instantaneously oxidized to red $[SiW_{11}Mn^{III}O_{39}]^{5-}$.[15,16] Since no oxidation occurs in the presence of water or pyridine, an inner-sphere electron-transfer process is suggested. Oxygenation of IV at −50 to −70 °C leads to a purple-red solution, but the color change is reversed by passage of N_2 for a few seconds. The cycle can be repeated at least 20 times. When $[GeW_{11}MnO_{39}]^{6-}$ is used instead of IV, the reversible color changes occur at higher temperatures. The oxygenated solutions are purple below −15 °C and green above that temperature. Both types of solution are converted to the original yellow Mn(II) solution by passage of N_2 for about 30 s, but at room temperature the green solution is slowly (h) irreversibly oxidized to red $[GeW_{11}MnO_{39}]^{5-}$.[17] The anhydrous yellow Mn(II) and purple oxygenated species have ESR spectra with hyperfine structure characteristic of mononuclear complexes (a(yellow), 86.3 G; a(purple), 88.5 G; see Figure 2). The ESR spectra are totally reproducible when oxygenation–deoxygenation is carried out at −15 °C. The major feature in both spectra occurs at $g \sim 4.3$, as expected for rhombic high-spin Mn(II) complexes,[18] but the ESR behavior is reminiscent of the Mn-porphyrin-O_2 adduct which was eventually interpreted to be a Mn(IV)–peroxo species.[19] Whether or not the heteropolyanion system is strictly analogous remains to be determined. In any case these complexes are the first examples of oxygen carriers that contain no organic ligands.

It is clear that the possibility of generating solutions of heteropolyanions in strictly anhydrous nonpolar solvents has opened up enormous new areas of chemistry and applications for these versatile substances. Besides the obvious implications for catalysis and molecular activation, we forsee the development of novel high-temperature chemistry, new methods of synthesis, and new polyanions and derivatives.

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(15) Since it is not possible to distinguish spectroscopically between five- and six-coordinate high-spin Mn(II) complexes, IV may contain coordinated Br^- (from the THpAB). We do not think this is likely in view of the behavior of I in toluene. Coordination of Br^- to the Mn(III) species is more probable; Knoth has reported $[PW_{11}O_{39}AlCl]^{5-}$ with Cl^- bound to Al(III) (Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 198).

(16) The product, extracted back into water, gave an identical absorption spectrum with that reported for $[SiW_{11}Mn(H_2O)O_{39}]^{5-}$. (Tourné, C. M.; Tourné, G. F.; Malik, S. A.; Weakley, T. J. R. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3875). An authentic sample of the latter anion, extracted into toluene and dehydrated with a stream of dry N_2, produced a solution with the same spectrum as the product of O_2 oxidation of IV.

(17) The reduction potential [Mn(III/II)] of the Ge-centered anion is 160 mV more positive than that of IV[16] and may account for the slower oxidation.

(18) Dowsing, R. D.; Gibson, J. F. *J. Chem. Phys.* **1969**, *50*, 294.

(19) Hoffman, B. M.; Wechsler, C. J.; Basolo, F. *J. Am. Chem. Soc.* **1976**, *98*, 5473. Hoffman, B. M.; Symanski, T.; Brown, T. G.; Basolo, F. *Ibid.* **1978**, *100*, 7253.

Kinetic Lactonization of 4,6-Dimethyl- and 2,4,6,8-Tetramethyl-5-hydroxyazelaic Acids: Ground-State Conformational Control

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The potential of symmetrical dilactones **1** and their derived keto diacids **2** for control of acyclic stereorelationships has been demonstrated.[2] It is clear that additional versatility would arise from processes that efficiently desymmetrize these molecules. One such operation, exemplified by the results described here, involves the use of a functional group that resides on a symmetry element to differentiate two (or more) symmetrically equivalent functionalities elsewhere within the same molecule. The specific, two-reaction sequence designed to achieve this goal was the reduction of the C(5) ketone (which lies on the C_2 axis of symmetry) of keto diacids **2** to an alcohol followed by acid-catalyzed lactonization of the hydroxyl group to either the C(1) or C(9) carboxylic acid, which generates the monolactone **4** or **5**, respectively.

Table I. Ratio[4] of *cis*-**4** to *trans*-**5**

	kinetic	thermodynamic
a	1:4.6	1:8.2
b	1:1.2	1:14.6
c	1:350[9]	1:4.2

Independent exposure of the *d,l*-di- and tetramethylated ketones **2a–c** to excess lithium in ammonia presumably generated the salts **3**.[3] Acidification to pH ~3 and rapid extraction did not allow isolation of the conjugate acids of **3** but instead led to kinetic ratios (see Table I) of the diastereomeric *cis*- and *trans*-5,6-disubstituted valerolactones **4** and **5**. If instead the salts **3** were acidified to pH ~1 or if the kinetically generated mixtures of **4** and **5** were reexposed to this stronger acid, a thermodynamic ratio (see Table I) of the isomers resulted. Similar thermodynamic ratios were obtained for the methyl esters corresponding to **4** and **5** (CH_2N_2) by their equilibration in absolute methanol catalyzed by Dowex acid resin.

The degree of kinetic stereoselectivity for each lactonization can be nicely explained on the basis of ground-state conformational control. Consider the four, reactive, chairlike,[5] preclosure conformations **6–9** under the assumption that the product-determining step is attack of the hydroxyl group on a protonated carboxylic acid.[6] Conformers **6** and **7** are related by a "ring-flip" and lead to the *cis*-5,6-disubstituted lactones **4**. The similarly related **8** and **9** lead to the trans lactones **5**.

In the case of **3a** (→**5a**:**4a** in 4.6:1), the conformation **6a** is not a viable reactant because of the 1,7-H_{Me},H_{Me} interaction.[7a,8] Conformer **9a**, which contains four 1,6-H,H interactions[7b] [H·

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(1) Procter and Gamble Fellow, 1982–1983. University of Minnesota Graduate School Dissertation Fellow, 1980–1981.

(2) Hoye, T. R.; Peck, D. R.; Trumper, P. K. *J. Am. Chem. Soc.* **1981**, *103*, 5618.

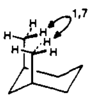
(3) Note that reduction of ketones **2a–c**, each of which possesses C_2 symmetry, can only generate a single alcohol (i.e., C(5) in **3** is achiral).

(4) This ratio was determined by integration of a capillary gas chromatogram of the methyl esters (CH_2N_2).

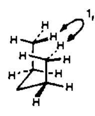
(5) It is unreasonable to consider boatlike reactant conformations since all involved atoms except the carboxyl carbon are sp^3 hybridized.

(6) The alternative possibility is that dehydration of the protonated tetrahedral intermediates corresponding to **6–9** is rate limiting. The subsequent analysis would still hold.

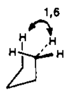
(7) (a) It is useful to identify the steric relationship that greatly destabilizes the diaxial form of *cis*-1,3-dimethylcyclohexane (i: Allinger, N. L.; Miller, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 2145) or the g^+g^- form of *n*-pentane (ii: Abe, A.; Jernigan, R. L.; Flory, P. J. *Ibid.* **1966**, *88*, 631. Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1966**, *44*, 3054. Sykora, S. *Coll. Czech. Chem. Commun.* **1968**, *33*, 3514) as a 1,7-interaction. Molecular arrangements incorporating 1,7-interactions over a set of nominally sp^3-hybridized atoms are necessarily attended by angle and/or torsional strain in order to alleviate spatial conincidence of the 1- and 7-atoms. (b) We similarly refer to butane gauchelike relationships (iii) as 1,6-interactions.



i



ii

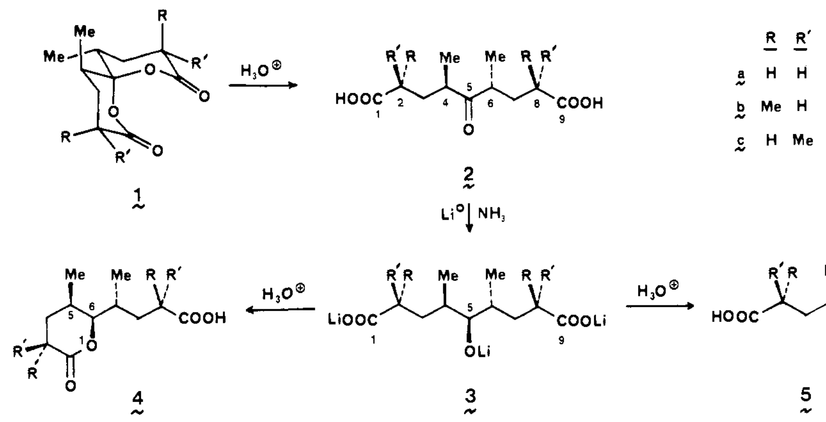


iii

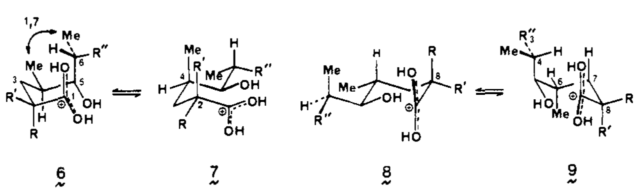
(8) Note that while 120° clockwise rotation about C(5)–C(6) removes the 1,7-H_{Me},H_{Me} interaction in **6**, it introduces new 1,7-interactions between the CH_2 in R″ and both the C(3)–H_{ax} and C(1)-O_{ax} atoms.

0002-7863/84/1506-2738$01.50/0

Scheme I



(4),H(7); H(6),H(3); C(5)-O*H*,*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.

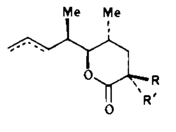


	R	R'	R''
a	H	H	CH_2CH_2COOH
b	Me	H	$CH_2CH(Me)COOH$
c	H	Me	"

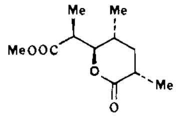
For **3b** (→**5b**:**4b** in 1.2:1) there is an identical number of 1,6-interactions in both **7b** and **8b**. Equal population of these preclosure conformations leads to the near unity kinetic ratio.

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**.

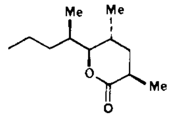
The stereochemical assignments for **1**–**5** were initially based upon extensive analysis of ^{1}H NMR data and the X-ray structure of dilactone **1b**.[2] Synthetic correlation to known compounds now supplements that evidence. Thus, oxidative decarboxylation (1.3 equiv of $Pb(OAc)_4$, 0.2 equiv $Cu(OAc)_2 \cdot H_2O$, 1.3 equiv of py, PhH, Δ)[10] of **5c** generated a mixture of olefins **10c** (~1:1), which was cleaved ($NaIO_4$, $RuCl_3 \cdot 3H_2O$) 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



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[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*

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

On page 7279 in the paragraph **Redox Potential of $(op)_2Cu^{2+}$** the following corrections should be made: $E^{\circ}_{O_2/O_2^-}$ should be −0.16 V rather than −0.33 V; $E^{\circ}_{(op)_2Cu^{2+}/(op)_2Cu^{+}}$ 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: $E^{\circ}_{(op)_2Cu^{2+}/(op)_2Cu^{+}}$ should be 0.11 V rather than −0.055 V.