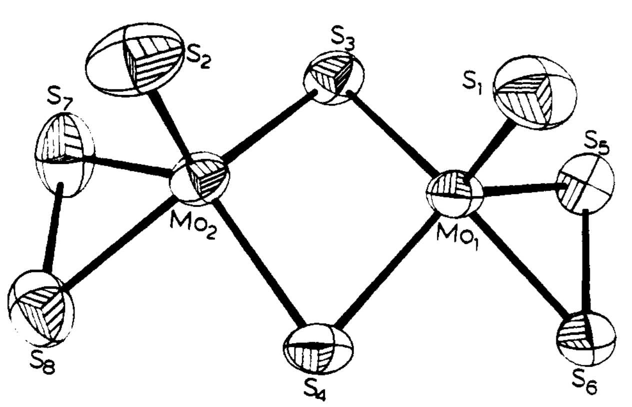

Figure 1. The structure of $Mo_2S_8^{2-}$ as determined in its $(C_6H_5)_4P^+$ salt. Bond distances and angles in the anion are: Mo_1–Mo_2 = 2.821 (1), Mo_2–S_2 = 2.108 (1), Mo_1–S_1 = 2.128 (1), S_5–S_6 = 2.051 (2), S_7–S_8 = 2.072 (3), Mo_2–S_7 = 2.391 (1), Mo_2–S_8 = 2.405 (2), Mo_1S_5 = 2.403 (1), Mo_1–S_6 = 2.375 (2), Mo_2–S_3 = 2.314 (1), Mo_2–S_4 = 2.313 (1), Mo_1–S_3 = 2.306 (1), Mo_1–S_4 = 2.308 (2) Å; S_4–Mo_2S_3 101.0 (1)°, S_4–Mo_1–S_3 101.4°, Mo_1–S_3–Mo_2 75.3 (1)°, Mo_1–S_4–Mo_2 75.2 (1)°.

$[(C_6H_5)_4P]_2[Mo_2S_8]$ in the dark. X-ray diffraction analysis[12-15] confirmed the presence of the binuclear $Mo_2(S)_2(\mu\text{-}S)_2(S_2)_2^{2-}$ ion shown in Figure 1. The complex anion is isostructural to the previously reported $Mo_2O_2(\mu\text{-}S)_2(S_2)_2^{2-}$ ion.[16,17] The *syn*-$Mo_2S_4^{2+}$ core has dimensions very close to those of related pentavalent dinuclear complexes.[18] The two disulfur ligands with S–S distances of 2.05 and 2.07 Å are, as in related complexes,[19] formulated as persulfide (S_2^{2-}) ligands.

The formation of $Mo_2S_8^{2-}$ from two MoS_4^{2-} anions involves a net two-electron oxidation with no overall gain or loss of sulfur atoms, i.e., $Mo_2S_8^{2-}$ is the dimer of the one-electron oxidation product of hexavalent MoS_4^{2-}. Despite this net oxidation, the $Mo_2S_8^{2-}$ product contains pentavalent Mo and belongs to the well-established class of pentavalent dinuclear complexes containing the $Mo_2O_xS_{4-x}^{2+}$ core (x = 0–4). Clearly, oxidation of the complex has caused reduction of the metal.

Reaction I can be fruitfully represented as involving induced internal electron transfer from S^{2-} to Mo(VI). Induced internal electron transfers in chemical systems had previously only been well established[8,20-22] for mononuclear cobalt complexes in which Co(III) is *reduced* to Co(II) upon reaction with an external one-electron *oxidant* such as Ce(IV). A concomitant net two-electron oxidation of the ligand is required (e.g., $C_2O_4^{2-} \rightarrow 2CO_2$). In the present case the external oxidant, RSSR, takes up two electrons and each of two Mo atoms takes up one electron. This requires, and we observe, a four-electron oxidation of the ligands, i.e., the conversion of four S^{2-} ligands to two S_2^{2-} ligands. The ease with which internal electron transfer occurs in this and related systems is a manifestation of the ability of sulfide/polysulfide ligand systems to exhibit energy levels both above and below the 4d levels of molybdenum.[23] This closeness of energy levels may also be responsible for the unusual reactivity of the related molecule $Mo_2O_2(\mu\text{-}S)_2(S_2)_2^{2-}$ toward activated alkynes,[24] which involves insertion of the alkyne into the $Mo(S_2)$ group forming a vinyl disulfide ring containing both Mo–C and S–C bonds.

The induced internal redox concept may be applied toward conceptual understanding of the remarkable reaction of MoS_4^{2-} with S_8 to yield MoS_9^{2-}.[6,7] Here, formation of the Mo(IV) product is viewed as a result of internal redox from S^{2-} to Mo(VI) induced by the external oxidant S_8. Clearly, in other multisulfidometal complexes, particularly where the metal is in a high formal oxidation state, the possibility of effecting net metal atom *reduction* by external *oxidants* must be considered.[25] Such manner of electronic structural and internal redox flexibility may be important in Mo enzymes such as nitrogenase and in Mo–S industrial catalysts.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths and bond angles, and structure factors (55 pages). Ordering information is given on any current masthead page.

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(12) The complete structure determination was carried out by Dr. C. S. Day of Crystalytics Co., Lincoln, NB.

(13) Crystal Data: space group $P\bar{1}$-C_1^1 (No. 2), with a = 13.277 (6) Å, b = 18.933 (9) Å, c = 10.959 (5) Å, α = 100.28 (4)°, β = 110.39 (4)°, γ = 104.23°, V = 2395 (2) Å^3, and Z = 2. Calculated density 1.56 g cm^{-3}. Unit cell dimensions were determined from least-squares refinement of 15 reflections with $2\theta > 25°$.

(14) The data was corrected for absorption (Ψ scan); transmission factors 0.718–1.000. The structure was solved using direct methods (SHELLxTL Direct Methods Programs), difference Fourier synthesis, and cascade block diagonal least-squares refinement. R_F = 0.043, Rw_F = 0.041 for 8126 independent diffracted intensities ($I > 3.0\sigma(I)$) with $3° < 2\theta < 55°$ (Mo Kα radiation). Anisotropic thermal parameters were utilized for all non-hydrogen atoms.

(15) Further details of the structure analysis, including tables of atomic coordinates, thermal parameters, bond lengths, bond angles, and structure factors, are available as supplemental material.

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(18) (a) Bunzey, G.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 682. (b) Huneke, J. T.; Enemark, J. H. *Ibid.* **1978**, *17*, 3698.

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(22) Holwerda, R. A.; Clemmer, J. S. *Inorg. Chem.* **1982**, *21*, 2103.

(23) Theoretical calculations by J. Bernholc of our laboratory (to be published) on $Mo_2S_8^{2-}$ confirm the delocalized nature of the highest filled and lowest empty orbitals in this complex.

(24) Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476.

(25) The reaction of MoS_9^{2-} with 2 equiv of $^-SCH_2CH_2S^-$ leads to the formation of MoS_4^{2-}. This reaction appears to be an example of an induced redox process in which an external *reductant* ($^-SCH_2CH_2S^-$) leads to *oxidation* of the Mo(IV) to Mo(VI) concomitant with reduction of the polysulfide ligands to sulfide ligands. It is, thus, an induced internal redox in the opposite sense (L → M) to that of equation I.

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pK_a and Keto–Enol Equilibrium Constant of Acetone in Aqueous Solution

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Received September 21, 1983
Revised Manuscript Received December 1, 1983

Recent interest in the chemistry of simple enols has led to a number of estimates of the keto–enol equilibrium constant for acetone in aqueous solution,[1,2] as well as the dissociation constant of this substance as a carbon acid in this medium.[2b,3,4] These estimates, however, are all necessarily approximate, for each depends upon an assumed value for at least one unknown quantity, e.g., the magnitude of a rate constant thought to be encounter controlled or the value of an unknown parameter in a thermodynamic cycle. We wish to report that we have now determined the keto–enol equilibrium constant as well as the acid dissociation

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(1) Dubois, J. E.; Toullec, J. *Tetrahedron* **1973**, *29*, 2859–2866. Dubois, J. E.; El-Alaoui, M.; Toullec, J. *J. Am. Chem. Soc.* **1981**, *103*, 5393–5401.

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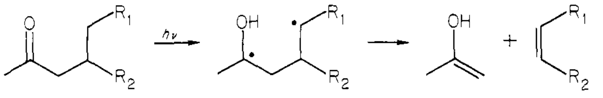
constant of acetone in aqueous solution by a method that requires no numerical assumptions.

Our method is based upon the fact that the ketonization of simple enols is base catalyzed and that this catalysis operates through conversion of the enol to the much more reactive enolate ion, eq. 1.[5] At sufficiently high hydroxide ion concentrations (ca.

$$CH_3C(OH){=}CH_2 + HO^- \overset{K}{\rightleftharpoons} CH_3C(O^-){=}CH_2 + H_2O \xrightarrow{k_o'} CH_3C(O)CH_3 + HO^- \quad (1)$$

0.01 M in the case of acetone enol), this catalysis becomes saturated, because the substrate is then essentially completely in the enolate form, and a suitable analysis of kinetic data obtained in this region produces values of both the equilibrium constant K, which is equal to the acid dissociation constant of the enol divided by the self-ionization constant of water, $K = K_a^E/K_w$, and the rate constant k_o'. Combination of the latter with the specific rate of hydroxide ion catalyzed enolization of acetone, k_{HO}^E, then gives the dissociation constant of the keto form of acetone as a carbon acid via the relationship $K_a^K = k_{HO}^E K_w/k_o'$. Since the ratio of these two acidity constants is the keto–enol equilibrium constant K_E, $K_a^K/K_a^E = K_E$; this analysis also provides a value of the latter quantity.

We generated the enol of acetone in alkaline aqueous solution by flash photolysis of appropriate ketone precursors. It is well known that Norrish type II photoelimination of ketones produces enols through γ-hydrogen transfer followed by fission of the α,β-carbon–carbon bond, eq 2.[6] We found that irradiation of



(2)

1

an aqueous solution of methyl isobutyl ketone (**1**, R_1 = H; R_2 = CH_3) (ca. 0.05 M) with a laser flash (frequency-quadrupoled Nd glass laser, 30 mJ/pulse at 265 nm, 20 ns pulse width at half-height)[7] gave acetone enol as a transient species with λ_{max} = 245 nm and a (pseudo) first-order decay whose lifetime was τ = 20 μs in 0.1 M NaOH. The same transient was also produced by similar irradiation of methyl propyl ketone (**1**, $R_1 = R_2$ = H) and methyl butyl ketone (**1**, R_1 = CH_3; R_2 = H), as required by the mechanism of eq 2.

Ketonization through the scheme of eq 1 is governed by the rate law given in eq 3. Figure 1 shows that data gathered in

$$\tau = k_o'^{-1} + ([H^+]/(k_o'K_a^E)) \quad (3)$$

sodium hydroxide solution over the concentration range $[HO^-]$ = 0.001–0.10 M at a constant ionic strength of 0.10 M (maintained through the addition of NaCl) conform to this law. Least-squares analysis of 54 data pairs gives the enol acidity constant $K_a^E = (1.09 \pm 0.07) \times 10^{-11}$ M, $pK_a^E = 10.96 \pm 0.03$, and the limiting rate constant $k_o' = (5.01 \pm 0.17) \times 10^4\ s^{-1}$.

Another, completely independent, estimate of pK_a^E may be made from the initial absorbances of the acetone enol transients, A_0, measured at λ = 245 nm. The dependence of these upon log $[H^+]$ describes a sigmoid titration curve with inflection point equal to pK_a^E, as expected since the enolate ion should absorb light much more strongly at this wavelength than the enol. Least-squares fitting of the data[8] to eq 4, in which ϵ_{EH} and ϵ_E are the molar

$$A_0 = \frac{\epsilon_{EH}[H^+] + \epsilon_E K_a^E}{[H^+] + K_a^E}[S]_{tot} \quad (4)$$

extinction coefficients of the enol and enolate ions and $[S]_{tot}$ is the total substrate (enol + enolate) concentration, gave pK_a^E = 10.83 ± 0.06. The small difference between this value and that obtained from the lifetime analysis described above indicates that systematic errors, not reflected in the statistical precision indexes given, are probably of the same order of magnitude as the latter. The weighted average of the two results, $pK_a^E = 10.94 \pm 0.08$,[9] is the best value of this quantity produced by the two independent methods used in this work.

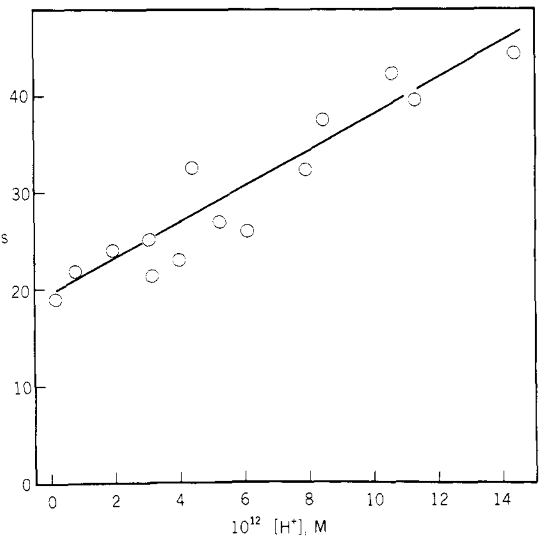


Figure 1. Relationship between hydrogen ion concentration and the lifetime of the transient species generated by flash photolysis of methyl isobutyl ketone in aqueous hydroxide ion solutions at 25.0 ± 0.1 °C and ionic strength = 0.10 M. The circles represent average values of τ at a given $[H^+]$.

The rate of enolization of acetone catalyzed by the hydroxide ion has been measured a number of times by halogen scavenging, but we now know, from the specific rate of ketonization determined here (k_o') and recent estimates of the scavenging rate constants,[3,4] that few of these previous studies were carried out at halogen concentrations sufficiently great to ensure that enolization was fully rate determining. We therefore made measurements ourselves, which give $k_{HO}^E = 0.220 \pm 0.005\ M^{-1}\ s^{-1}$ (ionic strength = 0.10 M).[10] Combination of this with the rate constant for the reverse reaction determined above, $k_o' = (5.01 \pm 0.17) \times 10^4\ s^{-1}$, then gives $K_a^K = k_{HO}^E K_w/k_o' = (6.96 \pm 0.27) \times 10^{-20}$ M, $pK_a^K = 19.16 \pm 0.02$.[12] Considering systematic errors as above, we arrive at $pK_a^K = 19.16 \pm 0.04$ for the dissociation constant of acetone ionizing as a carbon acid in aqueous solution at 25.0 °C.[9] This result shows that the traditional value, pK_a^K = 20,[14] was a reasonably good estimate, as are also the more recent approximations pK_a^K = 19.0 ± 1.3,[2b] 19.1 ± 0.5,[3] and 18.9 ± 0.3.[4]

The presently measured values of K_a^E and K_a^K lead to $K_E = (6.0 \pm 1.1) \times 10^{-9}$, $pK_E = 8.22 \pm 0.08$, as the keto–enol equilibrium constant for acetone in aqueous solution at 25.0 °C.[9] The best attempt to measure this constant by the classic bromine titration method led to the conclusion that it could not be determined by this technique but was less than 1×10^{-6}, $pK_E > 6$;[15]

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(7) The detection system was similar to that described by: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753. A detailed description will be given elsewhere: Hangarter, M. A.; Wirz, J., manuscript in preparation.

(8) Fiftyseven pairs of A_0 and $[H^+]$ measured in NaOH solutions and borax buffers at ionic strength = 0.10 M. Buffer data were not included in the lifetime analysis because the ketonization reaction is catalyzed to an appreciable extent by the buffer species in addition to hydroxide ion.

(9) This equilibrium constant is a *concentration quotient* at ionic strength = 0.10 M.

(10) This result is 30% greater than the value produced by a recent assessment[11] of literature data.

(11) Hine, J.; Kaufmann, J. C.; Cholod, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 4590–4595.

(12) In this calculation K_w was taken to be $1.59 \times 10^{-14}\ M^2$, on the basis of activity coefficients recommended by Bates.[11]

(13) Bates, R. G. "Determination of pH. Theory and Practise"; Wiley: New York, 1973; p 49.

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more recent approximate methods have put it at $pK_E = 7.2 \pm 0.9$[2a] and 8.5 ± 0.3.[1]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Swiss National Science Foundation (Project No. 2,470-82), and the Ciba Stiftung for their financial support of this research.

Total Synthesis of Bongkrekic Acid

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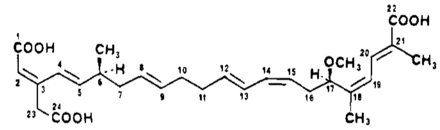
Adenosine triphosphate (ATP) from the oxidative phosphorylation of ADP in mitochondria can power eukaryotic cells only with the help of an ATP/ADP translocator protein that resides in the mitochondrial inner membrane.[1] Bongkrekic acid (**1**),[2,3] a toxin produced by the microorganism *Pseudomonas cocovenenans*, has a sufficiently high affinity for the translocator on the inside of this membrane to block effectively the export of ATP.[1b] Reported herein is the first chemical synthesis of **1**, a substance only difficultly available by fermentation, which serves as a useful biochemical reagent and which is of interest also from a structural and biosynthetic point of view.



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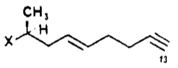

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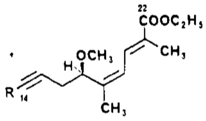
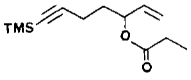
5, X = COOH
6, X = CH2OH



3, R = H
13, R = TIPS
15, R = Br



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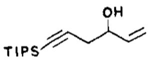

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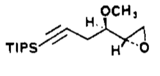

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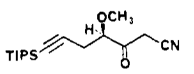

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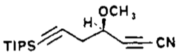

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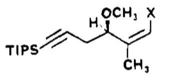
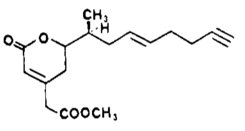


11, X = CN
12, X = CHO



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Retrosynthetic analysis led to the recognition of β-methylglutaconate (a possible biosynthetic component[4]), acetylenic aldehyde **2**, and acetylenic ester **3** as potentially useful synthetic precursors of **1**. The synthesis of **2**, corresponding to the C(5)–C(13) segment, was carried out as follows. 5-(Trimethylsilyl)(Me_3Si))-4-pentynal[5] and vinylmagnesium bromide in tetrahydrofuran (THF) at −78 °C gave a vinylcarbinol which was acylated with propionyl chloride–pyridine in methylene chloride at 0 °C to form **4** (80% overall). Propionate **4** was transformed into the acetylenic acid **5** (95% overall) by Claisen rearrangement of the *tert*-butyldimethylsilyl enol ether[6] at 50 °C followed by desilylation with 48% aqueous hydrofluoric acid in acetonitrile at 23 °C. The acid **5** was resolved as the ester with (*S*)-(+)-methyl mandelate by preparative HPLC on silica gel. The less polar diastereomer was reduced to the *l*-alcohol **6**, $[\alpha]^{23}_{\mathrm{D}}$ −3.4° (*c* 3, $CHCl_3$), which was oxidized by 1.4 equiv of pyridinium chlorochromate in methylene chloride in the presence of neutral alumina at 23 °C for 1.5 h to the aldehyde **2**, $[\alpha]^{23}_{\mathrm{D}}$ +16.2° (*c* 3.2, $CHCl_3$).[7]

The vinylcarbinol **7**, obtained by reaction of lithiated 1-(triisopropylsilyl (TIPS))propyne[8] with acrolein, was subjected to Sharpless epoxidation with kinetic resolution (1.0 equiv of titanium tetraisopropoxide, 1.1 equiv of diisopropyl D-(−)-tartrate and 1.5 equiv of *tert*-butylhydroperoxide at −20 °C for 16 h) to afford after chromatography on silica gel 80% (theoretical yield, 40% wt yield) of hydroxy epoxide of >90% optical purity,[9] $[\alpha]^{23}_{\mathrm{D}}$ +26.2° (*c* 1.3, EtOH), which upon treatment with sodium hydride–methyl iodide in THF at 20 ° yields 96% of *erythro*-methyl[9] epoxy ether **8**, $[\alpha]^{23}_{\mathrm{D}}$ +21.5° (*c* 1.3, EtOH). Reaction of **8** with 5 equiv. of sodium cyanide in ethanol at 35 °C for 10 h resulted in S_N2 displacement at methylene to form a single cyanohydrin (81% yield), which upon oxidation with diisopropylcarbodiimide (1.5 equiv)–excess dimethyl sulfoxide (Me_2SO)–dichloroacetic acid (0.5 equiv) at 0 °C for 0.5 h produced the keto nitrile **9** (93% yield), $[\alpha]^{23}_{\mathrm{D}}$ +42.7° (c 3.3, $CHCl_3$). The acetylene **10** was prepared from **9** by a novel two-step procedure: (1) reaction with sodium hydride at 23 °C in ether followed by 1.5 equiv of triflic anhydride (0 °C, 10 min) to form the enol triflate, (2) elimination (sodium hydride–ether–Me_2SO) at 0 °C for 0.5 h, overall yield of **10**, 65%, $[\alpha]^{23}_{\mathrm{D}}$ −60.5° (*c* 2, $CHCl_3$). Reaction of **10** with 2 equiv of dimethylcopperlithium in THF at −78 °C for 10 min followed by quenching (−78 °C) and isolation gave stereospecifically the (*Z*)-α,β-olefinic nitrile **11**, $[\alpha]^{23}_{\mathrm{D}}$ +118° (*c* 3, $CHCl_3$) (86%), which upon treatment with 1 equiv of diisobutylaluminum hydride in methylene chloride at −78 °C for 5 min afforded the *Z* aldehyde **12**, $[\alpha]^{23}_{\mathrm{D}}$ +73° (*c* 2.2, $CHCl_3$) (88%). Condensation of **12** with ethyl 2-triphenylphosphoranylidenepropionate in THF at 23 °C for 4 h produced **13**, $[\alpha]^{23}_{\mathrm{D}}$ +125.5° (*c* 2, $CHCl_3$) (96%) which was desilylated (1.2 equiv of tetrabutylammonium fluoride in THF at 23° for 1 hr) to form **3**, $[\alpha]^{23}_{\mathrm{D}}$ +32° (*c* 2, $CHCl_3$) (99%).

Elaboration of the aldehyde **2** to a predecessor of the C(1)–C(13) segment was accomplished by using a new method based

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(1) (a) Klingenberg, M. In "The Enzymes of Biological Membranes: Membrane Transport"; Martonosi, A. N., Ed.; Plenum Press: New York, 1976; Vol. 3, (b) Klingenberg, M. *Trends Biochem. Sci.* **1979**, *4*, 249.

(2) Structure: de Bruijn, J.; Frost, D. J.; Nugteren, D. H.; Gaudemer, A.; Lijmbach, G. W. M.; Cox, H. C.; Berends, W. *Tetrahedron* **1973**, *29*, 1541.

(3) Absolute configuration: Zyblir, J.; Gaudemer, F.; Gaudemer, A. *Experientia* **1973**, *29*, 648.

(4) Although the mode of biosynthesis of **1** has not been demonstrated, it is surmised that the two end segments, C(1)–C(4) and C(19)–C(22), originate from β-methylglutaconate (or equivalent) with C(5)–C(6) and C(17)–C(18) deriving from propionate and C(8)–C(16) deriving from five acetate units. In this scheme one carboxyl from β-methylglutaconate must be lost, leaving C(22) as terminal.

(5) Obtained from 4-pentyn-1-ol in 64% overall yield by the sequence (1) reaction with 2 equiv of *n*-butyllithium and then 2 equiv of Me_3SiCl, (2) O-desilylation with aqueous acid–THF, (3) oxidation with pyridinium chlorochromate in methylene chloride.

(6) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.

(7) The alcohol **6** obtained either directly from the mandelate ester or from the aldehyde **2** by reduction with sodium borohydride was shown to be of >90% optical purity by PMR analysis of the (−)-α-methoxy-α-(trifluoromethyl)phenylacetate (MTPA) ester: Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543. The configurational assignment for **6** was based on conversion to the ditrityl derivative[3] of 2-methyl-1,4-butanediol.

(8) Corey, E. J.; Rücker, Ch. *Tetrahedron Lett.* **1982**, *23*, 719.

(9) See: Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237 for procedure and analytical method.

(10) Corey, E. J.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 1851.

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