anionic triruthenium hydrocarbonyl cluster, $[HRu_3(CO)_{11}]^-$. After recovery of the organic (alcohol + diol) product fractions by distillation in vacuo, the solid residual catalysts display spectral bands characteristic[12] of $Ru(CO)_5$ and tetrabutylphosphonium bromide.[15] Recycle of this solid residue with additional syngas again gives rise to liquid product containing $[HRu_3(CO)_{11}]^-$. However, after multicycling, product solutions oftentimes evidence other ν_{CO} bands more typical of related polynuclear ruthenium hydrocarbonyls.[16-19] including $[H_3Ru_4(CO)_{12}]^-$, $[HRu_4(CO)_{13}]^-$ and $[HRu_6(CO)_{18}]^-$.

The ruthenium hydrocarbonyl cluster $[HRu_3(CO)_{11}]^-$, when evaluated as a model ruthenium catalyst precursor dispersed in Bu_4PBr (expt 4), exhibited comparable glycol productivity to other ruthenium catalyst precursors. The neutral hydrocarbonyl cluster $H_4Ru_4(CO)_{12}$ also performed well, but the $[Ru_6(CO)_{18}]^{2-}$ cluster proved less effective (expt 5). A series of runs with the RuO_2/Bu_4PBr couple plus various group 5B donor ligands[6] (expt 13-15), including phosphines, phosphites, and chelating (potentially tridentate,[20] tripod) ligands, as well as phosphine oxides favored in related glycol syntheses,[21] provided at best only modest improvements in glycol molar selectivity.

Other investigations into the factors favoring improved glycol productivity (Figure 1) indicate a linear dependence of oxygenate yield upon operating pressure and a sensitivity to feed gas composition. Although the stoichiometry of eq 1 calls for hydrogen-rich synthesis gas, an examination into the effect of CO/H_2 ratios upon glycol yield (Figure 1) suggests that 1:1 or CO-rich gas is preferable. This may be due in part to the need for high CO partial pressures to stabilize polynuclear ruthenium hydrocarbonyls at temperatures >200 °C. Increased hydrogen partial pressures generally favor improved alkanol production (Figure 1), possibly because of more facile hydrogenation capability or the presence of mononuclear ruthenium species that more readily catalyze methanol formation.[12] The situation is further complicated, however, by the fact that during each of these syntheses additional hydrogen is continually being generated in situ via competing, ruthenium-catalyzed, water-gas shift.[9,22]

Ruthenium catalysis, in contrast to homogeneous rhodium-catalyzed glycol synthesis,[1] appears to necessitate large quantities of bulky cation, such as the tetrabutylphosphonium cation, in order to achieve maximum glycol productivity. This appears true both for glycol synthesis via melt catalysis (Figure 1) and for the production of vicinal glycol esters.[6,8] Certainly the preferred Ru:P ratios of Figure 1 are contrary to any known charge ratio for either ruthenium hydrocarbonyl monomeric or cluster species. It likely reflects maximum solubility limits for the ruthenium species in the quaternary salt and/or the need to favor ion pairing.

The subsequent steps of CO hydrogenation to glycol may follow a hydroxymethylene growth reaction path as proposed earlier for rhodium homogeneous catalysis.[1] Our observed product distribution (ethylene glycol, glycol monoalkyl ethers, and ethanol, Table I), including the formation of trace quantities of propylene glycol, would be in keeping with the type of chain-growth scheme depicted here in eq 3[1,4] for ethylene glycol formation.

$$\mathrm{Ru(H)C{\equiv}O + H_2 \rightarrow {>}RuCH_2OH \xrightarrow{CO} {>}RuC({=}O)CH_2OH \xrightarrow{H_2} {>}RuCH(OH)CH_2OH \xrightarrow{H_2} HOCH_2CH_2OH} \quad (3)$$

(Hydroxymethyl)ruthenium intermediates have been proposed in related oxo catalysis[23] but isolated only for the earlier transition metals.[24] An alternative mechanstic scheme might involve formylruthenium clusters[25] or ruthenium coordinated to formaldehyde,[7] but in melt catalysis we find no enhancement in glycol productivity upon adding formaldehyde.

The extension of this unique fluid melt catalysis to related syntheses remains under study.

Acknowledgment. I thank Texaco Inc. for permssion to publish this paper, M. R. Swenson, R. Gonzales, T. D. Ellison, and D. W. White for experimental assistance, and Dr. J. L. Jackson for thermodynamic data.

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(14) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Suss, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1356.

(15) Residual solid ruthenium melt catalyst samples were also routinely subject to elemental analyses (5 elements), IR spectroscopy and m.p. determination (82-88 °). Data were consistent with the tetrabutylphosphonium bromide formulation. Dealkylation of the phosphonium salt did not appear to be a problem. Ruthenium analysis of these same solid catalyst samples showed no significant selective loss of ruthenium.

(16) Inkrott, K. E.; Shore, S. G. *Inorg. Chem.* **1979**, *18*, 2817.

(17) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc.*, Dalton *Trans.* **1980**, 383.

(18) Koepke, J. W.; Johnson, J. R.; Knox, S. A. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3947.

(19) Nagel, C. C.; Shore, S. G. *J. Chem. Soc., Chem. Commun.* **1980**, 530.

(20) DeBoer, J. J.; Van Doom, J. A.; Masters, C. *J. Chem. Soc., Chem. Commun.* **1978**, 1005.

(21) Kaplan, L. European Patent 0 006 634, 1980.

(22) Ford, P. C.; Rinker, R. G.; Ungermann, C.; Laine, R. M.; Landis, V.; Moya, S. A. *J. Am. Chem. Soc.* **1978**, *100*, 4595. Ford, P. C.; Ungermann, C.; Landis, V.; Moya, S. A.; Rinker, R. G.; Laine, R. M. *Adv. Chem. Ser.* **1979**. *No. 173*, 81.

(23) Sanchez-Delgado, R. A.; Bradley, J. S.; Wilkinson, G *J. Chem. Soc., Dalton Trans.* **1976**, 399.

(24) Casey, C. P.; Andrews, M. A.; McAlister, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 3378.

(25) Pruett, R. L.; Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *J. Organomet. Chem.* **1979**, *182*, C57.

Ligand-Induced Valence Tautomerism in Manganese–Quinone Complexes

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Received March 26, 1981
Revised Manuscript Received May 7, 1981

Recent studies have linked oxygen production by photosynthetic bacteria with a manganese-containing cofactor associated with photosystem II in plant chloroplasts.[1-6] Analytical results carried out to determine the number of chloroplast bound manganese atoms compared with data on the relative flash yield of O_2 suggest 3-4 functional Mn atoms per cofactor.[3,7] Other experiments seem to indicate the presence of Mn(II) and Mn(III) ions.[8,9] This has been confirmed by recent XAEFS/EXAFS experiments which further suggest that each Mn has a second transition-metal nearest neighbor, possibly a second Mn atom.[9,10] It is also known that 1,4-benzoquinones are included in the photosynthetic electron-transport chain,[11] although there is no direct evidence linking them to the Mn centers. Sawyer and co-workers have made some pertinent observations on the ability of manganese–catecholate complexes to reversibly bind molecular oxygen.[12,13] Reduction

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(1) Joliot, P.; Kok, B. In "Bioenergetics of Photosynthesis"; Govindjee, Ed.; Academic Press: New York, 1975.

(2) Mar, T.; Govindjee *J. Theor. Biol.* **1972**, *36*, 427-446.

(3) Cheniae, G. *Annu. Rev. Plant Physiol.* **1970**, *21*, 467-498.

(4) Earley, J. E. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 487-490.

(5) Renger, G., *Z. Naturforsch., Sect. B* **1970**, *B25*, 966-971.

(6) Olson, J. M. *Science* (Washington, DC) **1970**, *168*, 438.

(7) Govindjee; Wydrzynski, T.; Marks, S. B. In "Bioenergetics of Membranes"; Pacher, L., Papageorgious, G. C., Trebst, A., Eds.; Elsevier: Amsterdam, 1977.

(8) Rener, G. In "Photosynthetic Water Oxidation"; Metzer, H., Ed.; Academic Press: London, 1978.

(9) Sauer, K. *Acc. Chem. Res.* **1980**, *13*, 249-256.

(10) Kirby, J.; Robertson, A. S.; Smith, J. P.; Thompson, A. C.; Goodin, D. B.; Klein, M. unpublished work, quoted in ref 9.

(11) Crofts, A. R. In "Light-Induced Charge Separation in Biology and Chemistry"; Gerischer, H., Katz, J. J., Eds.; Dahlem Konferenzen: Berlin, 1979.

0002-7863/81/1503-3961$01.25/0

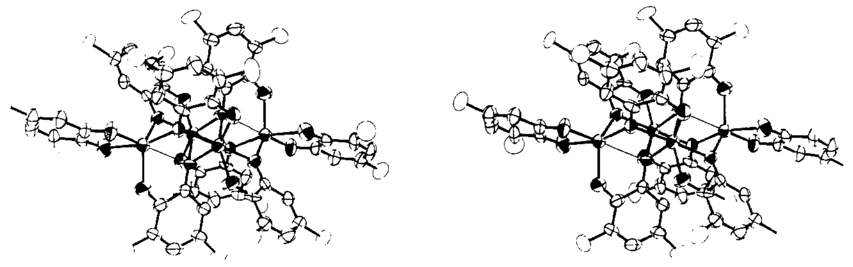

Figure 1. Stereoview of $Mn_4(3,5\text{-}DBSQ)_8$. Only the tertiary carbon atoms of the *tert*-butyl groups are shown.

of the bound dioxygen molecule occurs by intramolecular transfer of charge from a reduced quinone ligand. The viability of a manganese–quinone complex as a model for the photosynthetic manganese cofactor has been considered.[14] In such a system electrochemical activity of the metal is supplemented by the redox states of the quinone ligands. In this communication we present preliminary results on the synthesis and characterization of manganese complexes prepared with 3,5-di-*tert*-butyl-1,2-benzoquinone(3,5-DBQ). These complexes demonstrate the property of quinone ligands to modulate charge at the manganese center by intramolecular metal–ligand electron transfer.

A dark green moderately air-sensitive complex of composition $Mn[O_2C_6H_2(t\text{-}Bu)_2]_2$ was formed by irradiating a toluene solution of $Mn_2(CO)_{10}$ and 3,5-DBQ. The same product is obtained by treating $MnCl_2\cdot 4H_2O$ with the semiquinone form of the ligand, Na(3,5-DBSQ), in THF solution under Ar. In pyridine a purple adduct of composition $Mn[O_2C_6H_2(t\text{-}Bu)_2](py)_2\cdot 2py$ is obtained. A single-crystal molecular structure determination carried out on the parent complex has shown that it is a centrosymmetric tetramer.[15] A stereoview is shown in Figure 1. Manganese–oxygen lengths range from 2.062 (5) to 2.212 (6) Å, with one long Mn–O length of 2.526 (7) Å at the sixth coordination site of the end metal atoms of the figure. These metals show a clear distortion in coordination geometry toward a five-coordinate trigonal bypyramid. Bond lengths together with the structural features of the ligands point to a manganese(II) semiquinone formulation for the molecule, $Mn_4^{II}(3,5\text{-}DBSQ)_8$. Gross features are similar to Co(II) and Ni(II) complexes reported previously.[16] The tetramer has a magnetic moment of 5.1 μ_B per $Mn(3,5\text{-}DBSQ)_2$ unit in solid at room temperature, showing some evidence of intramolecular spin coupling. The pyridine adduct has a magnetic moment of 4.20 μ_B at 286 K in solid with little change in value down to 50 K. This is slightly greater than the spin-only moment for a $S = {}^3/_2$ metal ion. EPR spectra observed in either toluene solution at temperatures less than 200 K or in a solid sample cooled to liquid nitrogen temperature show several resonances in agreement with the expected fine structure of a $S = {}^3/_2$ species. This complex has also been characterized structurally[17] and a view of the centrosymmetric molecule is shown in Figure 2. Manganese–oxygen lengths of this molecule are 1.853 (2) Å, substantially different from lengths found in the tetramer and are consistent with Mn(IV). Carbon–oxygen lengths [1.349 (4) Å] and other structural features of the quinone ligands show that they are coordinated in the fully reduced catecholate form. Pyridine adduct formation has moved two electrons from the metal ions of the tetramer to the π^* level of the quinone ligands. Pyridine and bipyridine adducts have been prepared with the Co(II) and Ni(II) tetramers, $M_4(3,5\text{-}DBSQ)_8$, M = Co, Ni.[18,19] The nickel complexes are clearly Ni(II), $Ni(SQ)_2(py)_2$. With cobalt an equilibrium mixture of Co(II) and Co(III) species (eq 1) has been

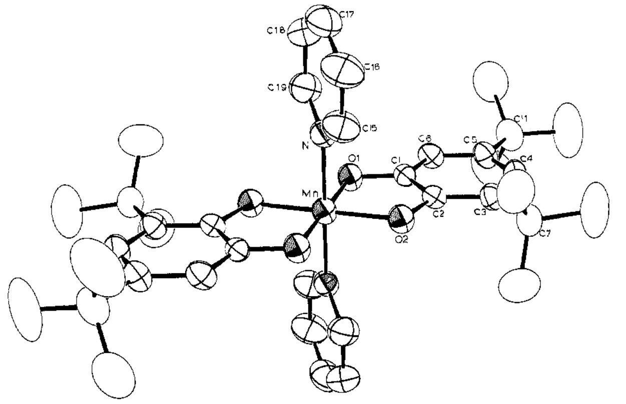

Figure 2. View of the centrosymmetric $Mn(3,5\text{-}DBCat)_2(py)_2$ molecule.

$$Co^{II}(SQ)_2(bpy) \rightleftharpoons Co^{III}(SQ)(Cat)(bpy) \qquad (1)$$

observed in solution. The Co(III) form prevails for $Co^{III}(3,5\text{-}DBSQ)(3,5\text{-}DBCat)(bpy)$ in solid.[18] In the present case full transfer of both electrons gives the Mn(IV) species, $Mn^{IV}(Cat)_2(py)_2$. Thermochromic behavior observed for $Mn(3,5\text{-}DBCat)_2(py)_2$ in toluene solution may point to valence tautomerism via metal–quinone electron transfer which is related to that observed for the cobalt complex. A toluene solution of the complex which is purple in solid is dark green at room temperature. The electronic spectrum of this solution closely resembles the Nujol mull spectrum of the parent tetramer. In the case of the cobalt complex, the spectrum of $Co^{II}(3,5\text{-}DBSQ)_2(bpy)$ was observed to be quite similar to $Co_4^{II}(3,5\text{-}DBSQ)_8$. At temperatures below 200 K the solution of $Mn(3,5\text{-}DBCat)_2(py)_2$ becomes dark purple, the color of the complex in solid. While further study will be required to understand these observations, it is possible that a two-step electron-transfer sequence exists including Mn(II), Mn(III), and Mn(IV) forms of the complex (eq 2).

$$Mn^{II}(SQ)_2(py)_2 \rightleftharpoons Mn^{III}(SQ)(Cat)(py)_2 \rightleftharpoons Mn^{IV}(Cat)_2(py)_2 \qquad (2)$$

Analytical data obtained on the air decomposition product of $Mn_4(3,5\text{-}DBSQ)_8$ indicate a product of formula $MnO_2(3,5\text{-}DBQ)_2$, although details of charge distribution and the nature of the O_2 ligand remain to be resolved. Dioxygen coordination is emerging as a general property of complexes containing reduced quinone ligands. Sawyer has reported reversible O_2 coordination to $Mn^{IV}(3,5\text{-}DBCat)_3^{2-}$ at a stoichiometry of one O_2 molecule per metal ion.[13] The neutral vanadium(IV) complex $V^{IV}(3,5\text{-}DBCat)_2$ adds O_2 reversibly with a $V{:}O_2$ ratio of 2:1.[20] Further characterization of $MnO_2(3,5\text{-}DBQ)_2$ will be required to determine the role that reduced quinone ligands play in O_2 fixation, but it is

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(12) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 989–991.

(13) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *Inorg. Chem.* **1980**, *19*, 492–496.

(14) Lawrence, G. D.; Sawyer, D. T. *Coord. Chem. Rev.* **1978**, *27*, 173–193.

(15) X-ray data for $Mn_4(3,5\text{-}DBSQ)_8$: Space group $P_{\bar{1}}$ triclinic; 2756 unique reflections $[F_o > 3\sigma (F_o^2)]$; $a = 14.822$ (9), $b = 14.803$ (4), $c = 16.428$ (6) Å; $\alpha = 118.19$ (2), $\beta = 110.63$ (3), $\gamma = 92.86$ (4)°; $V = 2869$ Å^3; $Z = 1$; $R_F = 0.059$, $R_{wF} = 0.063$.

(16) Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439–3444.

(17) X-ray data for $Mn(3,5\text{-}DBCat)_2(py)_2 2py$: Space group $P2_1/c$, monoclinic; 2429 unique reflctions $[F_o^2 > 3\sigma(F_o^2)]$; $a = 9.032$ (4), $b = 18.862$ (9), $c = 13.296$ (7) Å; $\beta = 96.54$ (4)°; $V = 2250$ Å^3; $Z = 2$; $R_F = 0.049$, $R_{wF} = 0.056$.

(18) Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951–4957.

(19) Lynch, M. W.; Buchanan, R. M.; Pierpont, C. G.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1038–1046.

(20) Wilshire, J. P.; Sawyer, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 3972–3973.

suspected that they serve as charge storage areas for O_2 reduction.

Acknowledgment. This work was supported by NIH Grant HL13652 to D.N.H. and NIH Grant GM23386 to C.G.P.

Supplementary Material Available: Tables of atomic positional and thermal parameters for both structures (3 pages). Ordering information is given on any current masthead page.

Stereocontrolled Synthesis of Cis-2,5-Disubstituted Tetrahydrofurans and *cis*- and *trans*-Linalyl Oxides

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Received March 5, 1981

The synthesis of polyether antibiotics is currently receiving considerable attention.[1] A particularly challenging aspect of this work is the stereocontrolled construction of the substituted tetrahydrofuran units found in many of these natural products, particularly those units in which there is a cis relationship between substituents at the 2 and 5 positions. An attractive method for the formation of substituted tetrahydrofurans is electrophilic cyclization of γ,δ-unsaturated alcohols, but the limited information available confirms the expectation that trans isomers are favored.[2] We reasoned that the desired cis-1,3 stereorelationship could be induced via two transient trans-1,2 relationships, by cyclizing olefinic ethers (as depicted in Scheme I). This proposal was supported by the observation of Allred and Winstein that the stereoisomers of 5-methoxy-2-hexyl brosylate solvolyze at different rates ($k_{\text{threo}} = 2.4k_{\text{erythro}}$) via analogous oxonium ion intermediates.[3] In fact, the cyclization of olefinic benzyl ethers with iodine does provide a general, highly stereoselective method for the synthesis of cis-2,5-disubstituted tetrahydrofurans, as indicated in Table I.[4]

Scheme I

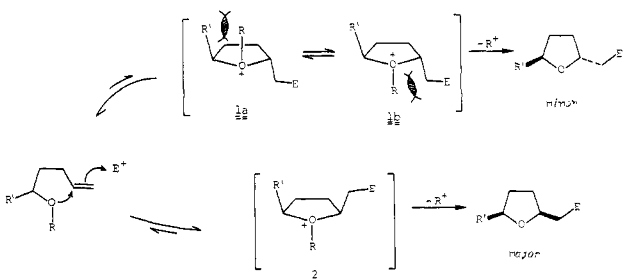
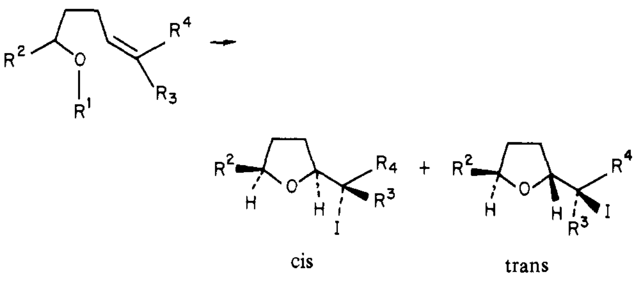


Table I. Iodocyclization of γ,δ-Unsaturated Ethers and Alcohols[a]



example	R^1	R^2	R^3	R^4	cis/trans ratio[c]	yield,[d] %
1	H	CH_3	H	H	0.5	66
2	CH_3	CH_3	H	H	0.5	15
3	CH_2Ph	CH_3	H	H	2	60
4	$SiMe_2$-*t*-Bu	CH_3	H	H	3	43
5	Si-*t*-$BuPh_2$	CH_3	H	H	8	30
6	BB[b]	CH_3	H	H	3.7	74
7	DCB[b]	CH_3	H	H	21	63
8	H	$(CH_3)_2CH$	H	H	0.25	88
9	DCB	$(CH_3)_2CH$	H	H	20	95[e]
10	H	CH_3	CH_3	H	0.5	99
11	DCB	CH_3	CH_3	H	25	75
12	H	CH_3	H	CH_3	0.4	81
13	DCB	CH_3	H	CH_3	12	47
14	CH_2Ph	CH_3	CO_2CH_3	H	6	55
15	DCB	CH_3	CO_2CH_3	H	50	60
16	BB	CH_3	CO_2CH_3	CH_3	10	44

[a] Reaction conditions: I_2, CH_3CN, 0 °C; with the following exceptions: $NaHCO_3$ included for alcohol substrates (examples 1, 8, 10, and 12); cyclizations performed at 21 °C for ester substrates (examples 14–16). [b] BB = 4-bromobenzyl; DCB = 2,6-dichlorobenzyl. [c] Ratio determined by ^{13}C or ^{1}H NMR spectroscopy. [d] Isolated yield of purified product after chromatography or bulb-to-bulb distillation, unless otherwise indicated. [e] Yield based on ^{1}H NMR spectroscopy.

We have gained a qualitative understanding of the factors involved in these cyclizations by studying a variety of derivatives of 5-hexen-2-ol (examples 1–7 in Table I). Loss of the alkyl group R from the oxonium ion intermediates **1** and **2** must be slow in comparison to reversal of their formation so that **2** will be favored thermodynamically and not just kinetically: the benzyl ether for example leads to only a 2:1 preference for cis (example 3). On the other hand, if loss of the alkyl substituent is too slow, side reactions such as cleavage of the other carbon–oxygen bond may ensue, which explains the poor yield which is obtained with the methyl ether (example 2).[3] The alkyl substituent must be bulky enough to exert a significant steric effect, but not so large as to prevent cyclization altogether; the silyl ethers cyclize with moderate selectivity but in poor yield (examples 4 and 5).[5] In the 2,6-dichlorobenzyl group is found the appropriate balance of electronic and steric properties for the 5-hexen-2-yl substrate (example 7). As a class, the substituted benzyl groups have the advantage that they can be tailored to fit the electronic needs of a variety of systems, as demonstrated by the other examples in Table I.

The stereochemistry of the 2-iodomethyl-5-methyltetrahydrofuran isomers was assigned by deiodination ($LiAlH_4$) to give the 2,5-dimethyl derivatives, whose ^{1}H NMR spectra have been reported.[6] The stereochemical assignments of the other 2,5-disubstituted tetrahydrofurans rest on analogy with this one and

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[†] Fellow of the Alfred P. Sloan Foundation, 1979–1981.

(1) Structures: Westley, J. W. *Annu. Rep. Med. Chem.* **1975**, *10*, 246. Westley, J. W. *Adv. Appl. Microbiol.* **1977**, *22*, 172–223. Pressman, B. C. *Annu. Rev. Biochem.* **1976**, *45*, 501–530. For references to initial synthetic work on nonactin, lasalocid A, and monensin, see: Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2–72. For more recent work on monensin, see: Collum, D. B.; MacDonald, J. H., III; Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2117–2121. Walba, D. M.; Edwards, P. D. *Tetrahedron Lett.* **1980**, 3531–3534. Lasalocid A: Ireland, R. E.; Thaisrivongs, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 1155–1157. Nonactic acid: Bartlett, P. A.; Jernstedt, K. K. *Tetrahedron Lett.* **1980**, 1607–1610. Ireland, R. E.; Vevert, J.-P. *J. Org. Chem.* **1980**, *45*, 4259–4260. Calcimycin (A-23187): Evans, D. A.; Sacks, C. E.; Kleschick, W. A.; Taber, T. R. *J. Am. Chem. Soc.* **1979**, *101*, 6789–6791. Grieco, P. A.; Williams, E.; Tanaka, H.; Gilman, S. *J. Org. Chem.* **1980**, *45*, 3537–3539.

(2) Brown, H. C.; Geohegan, P. J., Jr.; Kirek, J. T.; Lynch, G. J. *Organometl. Chem. Synth.* **1970/1971**, *1*, 7–22. Hosokawa, T.; Hirata, M.; Murahashi, S.-I.; Sonoda, A. *Tetrahedron Lett.* **1976**, 1821–1824. Tanaka, O.; Tanaka, N.; Ohsawa, T.; Iitaka, Y.; Shibata, S. *Tetrahedron Lett.* **1968**, 4235–4238.

(3) Allred, E. L.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 3991–3997. The explanation of their results (as well as the ones we report here) may rest on more subtle interactions than those depicted in Scheme I, since the oxonium ion is only slightly pyramidal. A Kos and P. v. R. Schleyer, for example, have shown (using MNDO calculations) that the methyl group of *O*-methyltetrahydrofuran cation lies out of the C_2–O–C_5 plane by only 8.5° and the inversion barrier is of the order of 0.1 kcal/mol (personal communication).

(4) Satisfactory spectra and combustion analyses were obtained for all new compounds. Stereoisomers were not separated before characterization.

(5) Addition of iodine itself to the double bond competes with cyclization of these silyl ethers; hence the reaction cannot be driven to completion by the addition of more reagent or by prolonged reaction times.

(6) Gagnaire, D.; Monzeglio, P. *Bull. Soc. Chim. Fr.* **1965**, 474–480.

0002-7863/81/1503-3963$01.25/0