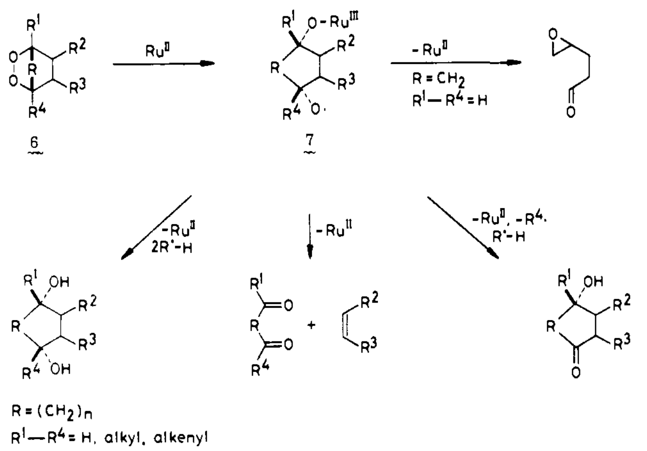
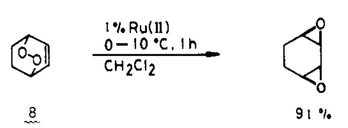
Scheme I



(10 equiv) produced acetone in 39% yield.[16] Therefore the 4-hydroxy ketone products may be formed from the initially produced 1,4-diols.[17]

The oxy radical can interact with a carbon–carbon double bond present in the substrate. As illustrated in eq 5 and 6, $RuCl_2(PPh_3)_3$



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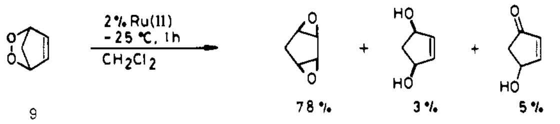

(6)

catalyzes smoothly the isomerization of 2,3-unsaturated 1,4-epiperoxides to the 1,2,3,4-diepoxides, which provides a useful synthetic tool.[18]

Thus the Ru(II)-catalyzed reactions involve radical intermediates, but they behave differently from free diradicals formed by photolysis or thermolysis of the epiperoxides.[19] The Ru atom affects profoundly the stability and reactivity of the radicals through interaction with the oxygen atom, allowing selective transformations under mild conditions. The selectivity profile is different from the related Fe(II)-promoted reaction, which proceeds via free-radical intermediates generated by an outer-sphere electron-transfer process.[20]

Acknowledgment. We thank Drs. Y. Naya and H. Naoki of Suntory Institute for Bioorganic Research for the 360-MHz NMR measurement. We are also indebted to Professor S. Suzuki of our Department for the suggestion for the malonaldehyde assay.

Registry No. 1, 280-53-5; **2**, 5718-73-0; **3**, 279-35-6; **4**, 63942-75-6; **5**, 79171-56-5; $RuCl_2(PPh_3)_3$, 15529-49-4; butanedial, 638-37-9; ethene, 74-85-1; *cis*-1,4-cyclohexanediol, 731-71-5; 4-hydroxycyclohexanone, 13482-22-9; 6-methyl-2,5-heptanedione, 13901-85-4; 4-hydroxy-4-methylcyclohexanone, 17429-02-6; *cis*-4-isopropyl-1-methyl-1,4-cyclohexanediol, 17948-61-7; propanedial, 542-78-9; 3-oxiranepropanal, 65842-25-3; *cis*-1,3-cyclopentanediol, 16326-97-9.

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[16] In the absence of epiperoxides, secondary alcohols are inert to the Ru(II) complex under the present reaction conditions. Treatment of 2-propanol with 5 mol % of $RuCl_2(PPh_3)_3$ (CH_2Cl_2, 25 °C/16 h and then 50 °C/2.5 h) did not produce acetone; addition of 2-cyclohexenone to this system did not afford cyclohexanone either.

[17] $RuCl_2(PPh_3)_3$ liberates triphenylphosphine ligands in solution: Pri-Bar, I.; Buchman, O.; Schumann, H.; Kroth, H. J.; Blum, J. *J. Org. Chem.* **1980**, *45*, 4418 and references cited therein. The phosphine does react with cyclic peroxides; reaction with saturated epiperoxides produces the diols, whereas reaction with 2,3-unsaturated 1,4-epiperoxides affords 1,3-diene 1,2-epoxides. However, under the present catalytic conditions, it does not participate in the product formation to any great extent.

[18] For the Co(II)-*meso*-tetraphenylporphine-catalyzed reaction see ref 4e.

[19] For instance, thermolysis of **3** in CD_2ClCD_2Cl at 73 °C gives a mixture of 4,5-epoxypentanal (54%), levulinaldehyde (42%), and 2,3-dioxabicyclo[2.2.1]heptane (4%): Salomon, R. G.; Salomon, M. F.; Coughlin, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 660. For the thermolysis of **1**, see ref 8 and Bloodworth (Bloodworth, A. J.; Baker, D. S. *J. Chem. Soc., Chem. Commun.* **1981**, 547). For the thermolysis of **2**, see: Moore, C. G. *J. Chem. Soc.* **1951**, 234. Thermolysis of **9** produces (*Z*)-4,5-epoxy-2-pentenal (58%) and the *syn*-diepoxide (7%): Schülte-Elte, K. H.; Willhalm, B.; Ohloff, G. *Angew. Chem.* **1969**, *81*, 1045. Photolysis of **8** gives the *syn*-diepoxide (27%) and 3,4-epoxycyclohexanone (22%): Maheshwari, K. K.; de Mayo, P.; Wiegand, D. *Can. J. Chem.* **1970**, *48*, 3266.

[20] Reaction of **2** and $FeSO_4$ gives 4-hydroxy-4-methylcyclohexanone (93%) and propane (99%).[3b]

Square and Butterfly, 12-Electron Mo_4 Clusters Formed by Coupling $\mathrm{Mo{\equiv}Mo}$ Bonds

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Received October 29, 1981

One of the several reaction pathways potentially available to compounds with metal-to-metal multiple bonds is condensation or oligomerization to give cluster compounds with delocalized metal-to-metal bonding. McCarley and co-workers reported[1] the dimerization of two $(\mathrm{Mo}\overset{4}{—}\mathrm{Mo})^{4+}$ units to give a rectangular Mo_4 cluster with alternating Mo–Mo triple and single bonds. We wish now to report reactions in which square and butterfly 12-electron Mo_4 clusters are formed from the coupling of $\mathrm{Mo{\equiv}Mo}$ bonds.

Hydrocarbon solutions of $Mo_2(O\text{-}i\text{-}Pr)_6$ $(\mathrm{M{\equiv}M})$[2] react with CH_3COX (X = Cl and Br) to give isopropylacetate and haloalkoxy molybdenum compounds.[3] When the reactions are carried out in hexane, black crystalline compounds of formula $Mo_4X_3(O\text{-}i\text{-}Pr)_9$[4] crystallize from a cooled solution (ca. −5 °C) and have been obtained in 70% yield according to eq 1.

$$2Mo_2(O\text{-}i\text{-}Pr)_6 + 3MeCOX \rightarrow Mo_4X_3(O\text{-}i\text{-}Pr)_9 + 3MeCOO\text{-}i\text{-}Pr \quad (1)$$

The ^1H NMR spectra of $Mo_4X_3(O\text{-}i\text{-}Pr)_9$ compounds are quite remarkable: there are five methyne septets in the ratio 2:2:2:2:1 and nine partially overlapping doublets for the methyl resonances. This can be explained as follows. Halo-for-alkoxy group exchange increases the Lewis acidity of the metal atoms, and the compounds "$Mo_2X_2(O\text{-}i\text{-}Pr)_4$" once formed associate with their precursors $Mo_2X(O\text{-}i\text{-}Pr)_5$. Association by the formation of one alkoxy and three halide bridges to give I has a precedent in the structures of $Mo_4(\mu\text{-}F)_4(O\text{-}i\text{-}Bu)_8$ and $Mo_4(\mu\text{-}F)_3(\mu\text{-}NMe_2)(O\text{-}t\text{-}Bu)_8$.[5] It is not necessary to invoke delocalized metal–metal bonds: there are merely two isolated $\mathrm{Mo{\equiv}Mo}$ bonds brought into close proximity by the bridging ligands. Note that I has C_2 symmetry, which accounts for the presence of five types of isopropyl groups and the appearance of nine isopropyl methyl groups, since the four different pairs of OR ligands each have diastereotopic methyl groups.

$Mo_4X_3(O\text{-}i\text{-}Pr)_9$ compounds react further with CH_3COX to give $Mo_4X_4(O\text{-}i\text{-}Pr)_8$ compounds (X = Cl or Br), which are es-

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[1] (a) McGinnis, R. N.; Ryan, T. R.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 7900. (b) McCarley, R. E.; Ryan, T. R.; Torardi, C. C. *ACS Symp. Ser.* **1981**, *155*, 41.

[2] Chisholm, M. H.; Cotton, F. A.; Extine, M. W. Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

[3] All reactions were carried out by using dry and oxygen-free solvents and atomospheres (N_2). Additions of acetyl chloride were made by use of a calibrated vacuum manifold.

[4] Satisfactory elemental analytical data have been obtained.

[5] Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7100.

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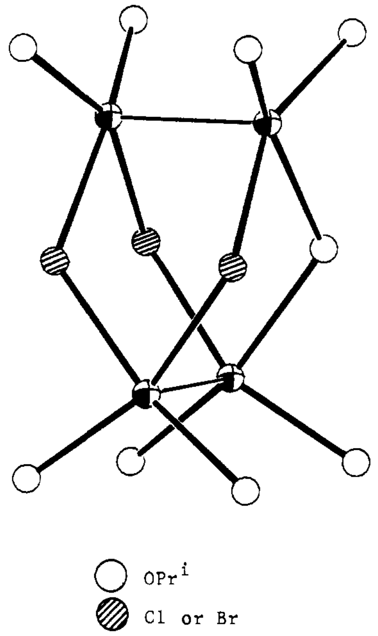

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sentially insoluble in hexane and toluene. A direct synthesis of $Mo_4X_4(O\text{-}i\text{-}Pr)_8$ in toluene is thus possible, and based on the basis of eq 2, $Mo_4X_4(O\text{-}i\text{-}Pr)_8$ compounds have been obtained in ca. 60% yield.

$$2Mo_2(O\text{-}i\text{-}Pr)_6 + 4MeCOX \rightarrow Mo_4X_4(O\text{-}i\text{-}Pr)_8 + 4MeCOO\text{-}i\text{-}Pr \quad (2)$$

In the space group $I4/m$, $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$ lies on the crystallographic 4-fold axis.[6] The two atoms Cl(3) and Mo(1) lie on this axis and are related to Mo(1D) and Cl(3D) by the crystallographic mirror plane at $Z = {}^1/_2$. The two remaining molybdenum atoms are systematically disordered about the 4-fold axis, giving an apparent Mo_6 octahedral moiety with the molybdenum atoms in the plane (and their corresponding chloride ligands) having an occupancy of 0.50. Packing considerations indicate the square structure shown in Figure 1 and reveal an interesting "layered" disorder. The molecule has absolute C_{2h} symmetry and virtually D_{4h} symmetry. The departure from the latter, we believe, is merely due to molecular packing and arrangements of isopropyl groups. The local $MoClO_4$ geometry corresponds to a square-based pyramid.

If for each metal atom we define the z axis coincident with the Mo–Cl bond and the x axis in the Mo_4 plane, then each molybdenum may use its p_z atomic orbital to form Mo–Cl bonds and its s, p_x, p_y, d_{xy} atomic orbitals to form four Mo–O bonds, which leaves $d_{x^2-y^2}$, d_{xz}, d_{yz}, and d_{z^2} available for cluster M–M bonding. If the available 12 electrons are placed in bonding molecular orbitals, then an average M–M bond order of 1.5 is attained. $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$ is diamagnetic, and the observed Mo–Mo distance 2.378 (1) Å is certainly consistent with delocalized M–M bonding where the average M–M bond order is greater than 1. Compare, for example, the Mo–Mo single-bond distances in $Zn_2Mo_3O_8$ (2.524 (2) Å)[7] or $Mo_3O(ONe)_{10}$ (2.529 (9) Å)[8] where six electrons are delocalized over three Mo–Mo bonds.

$Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ is very sparingly soluble in toluene, and in toluene-d_8 gave a ^1H NMR spectrum indicative of three types of O-i-Pr ligands in the integral ratio 4:2:2. This is inconsistent with the adoption of a structure akin to that found for $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$, and consequently a crystalline sample was obtained for an X-ray study.

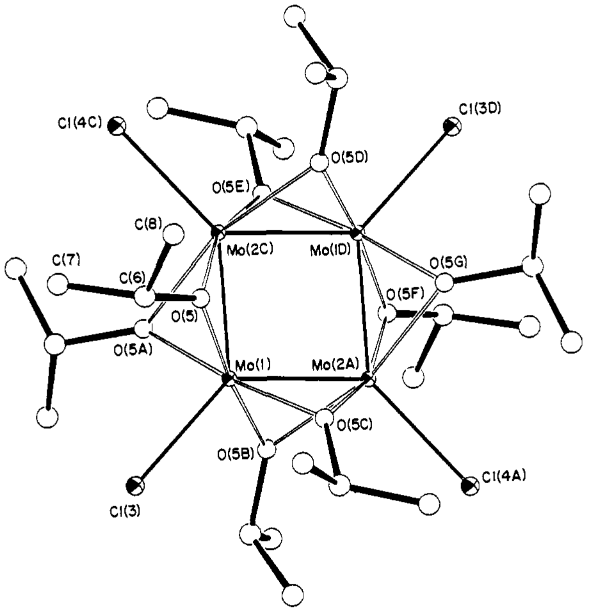

Figure 1. View of the $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$ molecule. The molecule has a crystallographically imposed C_2 axis, which contains Cl(3)–Mo(1)–Mo(1D)–Cl(3D), and a mirror plane, which contains Cl(4C)–Mo(2C)–Mo(2A)–Cl(4A) and relates the atoms O(5) and O(5D), O(5A) and O(5E), etc. Pertinent bond distances (Å) and angles are Mo(1)–Mo(2A) = Mo(1)–Mo(2C) = 2.378 (2), Mo(1)–Cl(3) = 2.442 (5), Mo(1)–O(5) = 1.981 (4), Mo(2C)–O(5) = 2.078 (4), Mo(2C)–Mo(1)–Mo(2A) = 91.4 (1)°, Mo(1)–Mo(2C)–Mo(1D) = 88.5 (1)°, O(5)–Mo(1)–O(5C) = 89.8 (1)°, O(5)–Mo(1)–O(5B) = 173.4 (1)°, O(5)–Mo(1)–Cl(3) = 93.3 (1)°, O(5)–Mo(1)–Mo(2C) = 56.0 (1)°, O(5)–Mo(1)–Mo(2A) = 118.6 (1)°, Mo(1)–O(5)–Mo(2C) = 71.7 (1)°, Mo(1)–O(5)–C(6) = 136.8 (1)°, Mo(2C)–O(5)–C(6) = 138.7 (1)°.

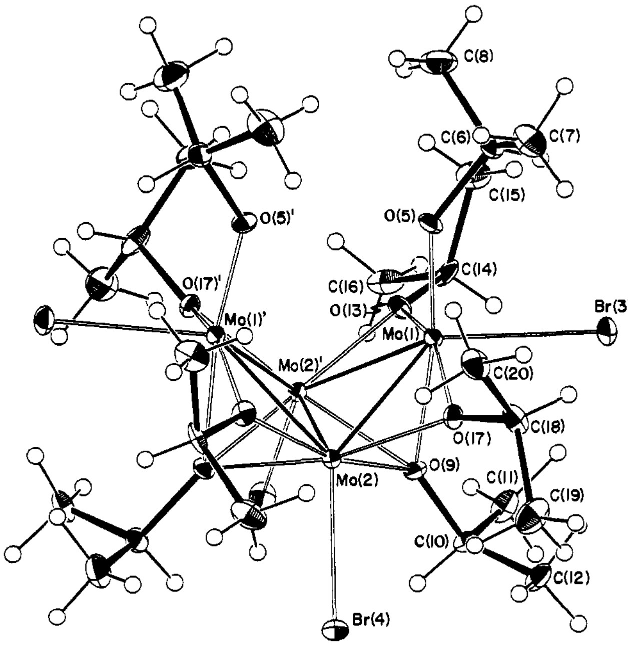

Figure 2. ORTEP view of the $Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ molecule. Some pertinent bond distances (Å) and angles (deg) are as follows: Mo(1)–Mo(2) = 2.513 (1); Mo(2)–Mo(1)′ = 2.516 (1); Mo(2)–Mo(2)′ = 2.481 (1); Mo(1)–Br(3) = 2.596 (1); Mo(2)–Br(4) = 2.568 (1); Mo(1)–O(5) = 1.84 (1); Mo(1)–O(5) = 1.84 (1); average Mo–μ–O = 2.02 (2); average Mo–μ_3-O = 2.15 (1); Mo(1)–Mo(2)–Mo(1)′ = 81.6 (1); Mo(1)–Mo(2)–Mo(2)′ = 60.5 (1); Br(3)–Mo(1)–O(5), –O(13), –O(9), –O(17) = 93.6 (1), 94.1 (1), 94.9 (1), 90.7 (1); Br(4)–Mo(2)–O(9), –O(9)′, –O(13), –O(17) = 88.9 (1), 89.7 (1), 106.7 (1), 105.2 (1).

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[6] Crystal data for $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$ at −162 °C: space group = $I4/m$, $a = b = 9.97$ (1) Å, $c = 18.27$ (2) Å, $Z = 2$, $d_c = 1.825$ g cm^{-3}. Of the 846 unique reflections collected with use of Mo Kα radiation, $5° \leq 2\theta \leq 50°$, the 592 having $F > 2.33\sigma(F)$ were used in the full-matrix refinement. Final residuals are $R_F = 0.045$ and $R_{wF} = 0.040$.

[7] Ansell, G. B.; Katz, L. *Acta Crystallogr.* **1966**, *21*, 482.

[8] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *J. Am. Chem. Soc.* **1981**, *103*, 5967.

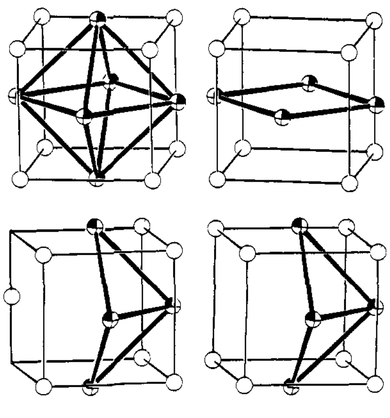

Figure 3. Cube–octahedral relationship found in $Mo_6(\mu_3\text{-}X)_8^{4+}$ compounds (top left); Mo_4O_8 moiety in $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$ (top right); Mo_4O_8 moiety in $Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ (bottom right); $Mo_4I_7^{2+}$ moiety in $Mo_4I_{11}^{2-}$ (bottom left).

In the crystal,[9] the $Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ molecule has C_{2v} symmetry. The four molybdenum atoms form a "butterfly" or opened tetrahedron with five short Mo–Mo distances, 2.50 Å (averaged), and one long Mo–Mo distance, 3.287 (1) Å. A view of the molecule is given in Figure 2. In contrast to the $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$ molecule, which has eight equivalent μ_2-O-*i*-Pr ligands, there are a pair of symmetry related terminal O-*i*-Pr ligands, a pair of symmetry related μ_3-O-*i*-Pr ligands, and four equivalent μ_2-O-*i*-Pr ligands. The four bromide ligands are terminal. The five short Mo–Mo distances, 2.50 Å (averaged), are longer than the four equivalent Mo–Mo distances, 2.387 (1) Å, in $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$.

The structures of $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$ and $Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ are, however, closely related to one another. Both contain Mo_4 units within a cube of O-*i*-Pr ligands and as such may be viewed as fragments of the well-known $Mo_6(\mu_3\text{-}X)_8^{4+}$ unit.[10] The $Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ structure may also be compared with the $Mo_4I_{11}^{2-}$ structure reported by McCarley et al.[11] The latter also contains a "butterfly" Mo_4 unit with five short Mo–Mo distances, 2.58 Å (averaged), and one long Mo–Mo distance, 3.035 (5) Å. This too may be viewed as a derivative of the $Mo_6(\mu_3\text{-}X)_8^{4+}$ unit: the central $Mo_4I_7^{2+}$ unit contains six I^- ligands at the corners of the cube, while the seventh bridges the two weakly bonded (nonbonded) molybdenum atoms (Mo–Mo = 3.035 (5) Å) at the midpoint of the edge of the idealized I_8 cube. These relationships to the $Mo_6(\mu_3\text{-}X)_8^{4+}$ unit are shown in Figure 3. In $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$, $Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ and $Mo_4I_{11}^{2-}$, there are four Mo-halide bonds directed along lines radiating from the center of the idealized X_8 cube.

McCarley noted:[11] "In C_{2v} symmetry, the Mo–Mo bonding in $Mo_4I_{11}^{2-}$ can be described as $(3a_1 + a_2 + b_1 + b_2)_b^{12}\ (a_2 + b_1)^3$. The latter $a_2 + b_1$ orbitals involve mainly interactions at the distance 3.035 (5) Å between d orbitals lyings in planes perpendicular to the Mo(1)–Mo(2) axis. These orbitals should have neither strongly bonding or antibonding character." It seems that we have now verified this qualitative MO description, since the $Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ molecule has only 12 electrons available for metal–metal bonding.

Finally, we noted that for the series of compounds of formula $Mo_4X_4(OR)_8$ we have found a bisphenoid of four molybdenum atoms with two localized Mo≡Mo bonds for X = F and R = *t*-Bu, and square Mo_4 unit with delocalized M–M bonds of order 1.5 for X = Cl and R = *i*-Pr, and a "butterfly" Mo_4 unit for X = Br and R = *i*-Pr, all of which readily accommodate 12 electrons in metal–metal bonds. Clearly for Mo≡Mo bonds, two plus two gives four, in more ways than one! Though to our knowledge there are no other square 12-electron M_4 cluster compounds, there are square $Cu(I)_4$ (d^{10}) compounds of formula $Cu_4(\mu\text{-}X)_4$.[12,13] Tetrahedral,[14] rectangular,[15] rhombohedral,[16] "butterfly",[11] and now square Mo_4 clusters are known.

Many questions are raised and further studies are in progress.[17]

Registry No. $Mo_4Cl_4(O\text{-}i\text{-}Pr)_8$, 80878-94-0; $Mo_4Br_4(O\text{-}i\text{-}Pr)_8$, 80878-95-1; $Mo_4Cl_3(O\text{-}i\text{-}Pr)_9$, 80890-28-4; $Mo_4Br_3(O\text{-}i\text{-}Pr)_9$, 80890-29-5; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; CH_3COCl, 75-36-5; CH_3COBr, 506-96-7.

Supplementary Material Available: Listings of fractional coordinates and isotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(9) Crystal data for $Mo_4Br_4(O\text{-}i\text{-}Pr)_8$ at −160 °C: space group *A*2/*a*, $a = 20.042$ (5) Å, $b = 10.980$ (2) Å, $c = 18.602$ (4) Å, $\beta = 112.60$ (1)°, $Z = 4$, $d_c = 2.067$ g cm^{-1}. Of the 3338 unique reflections collected with use of Mo Kα radiation, $6° \le 2\theta \le 50°$, the 2963 having $F > 2.33\sigma(F)$ were used in the full-matrix refinement. Final residuals are $R_F = 0.0376$ and $R_{wF} = 0.0363$.

(10) Schafer, H.; von Schnering, H. G. *Angew. Chem.* **1971**, *385*, 75. Guggenberger, L. J.; Sleight, A. W. *Inorg. Chem.* **1969**, *8*, 2041. Healy, P. C.; Kepert, D. L.; Taylor, D.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1973**, 646.

(11) Stensrad, S.; Helland, B. J.; Babich, M. W.; Jacobson, R. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 6257.

(12) X = CH_2SiMe_3: Jarvis, J. A. J.; Kilbourn, B. T.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 475.

(13) X = O-*t*-Bu: Greiser, T.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142.

(14) $Mo_4S_4X_4$ compounds (X = Cl, Br, I) contain a central Mo_4S_4 cube and a tetrahedral Mo_4 unit with Mo–Mo distances of 2.80 Å: Perrin, C.; Chevrel, R.; Sergent, M. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1975**, *280*, 949.

(15) $Mo_4Cl_8L_4$ (L = phosphine): ref 1a.

(16) $Ba_{1.13}Mo_8O_{16}$: ref 1b.

(17) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the Marshal H. Wrubel Computing Center, and the taxpayers of Indiana for financial support of this work. We are also grateful to Dr. Peter Thornton, Queen Mary College, London University, for carrying out magnetic susceptibility measurements.

Carbohydrates in Organic Synthesis. Synthesis of 16-Membered-Ring Macrolide Antibiotics. 5.[1] Total Synthesis of *O*-Mycinosyltylonolide: Synthesis of Key Intermediates

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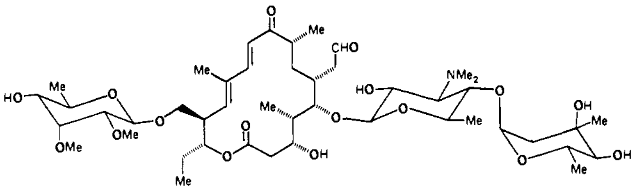
Received October 20, 1981

Tylosin (**1**)[2,3] is one of the most important and complex macrolide antibiotics of the 16-membered-ring family and is extensively used today as both a nutrient and a therapeutic agent.[4] In continuing our studies in the utilization of carbohydrates in organic synthesis[5] and in particular the synthesis of macrolide antibiotics,



1. Tylosin

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† Fellow of the A. P. Sloan Foundation, 1979–1983; recipient of a Camille and Henry Dreyfus Teacher-Scholar Award, 1980–1985.

(1) (a) Part 3: Nicolaou, K. C.; Seitz, S. P.; Pavia, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 1222. (b) Part 4: Nicolaou, K. C.; Pavia, M. R.; Seitz, S. P. *Ibid.* 1224.

(2) Isolation: Hamill, R. L.; Haney, M. E., Jr.; Stamper, M.; Wiley, P. F. *Antibiot. Chemother.* (*Washington, D.C.*) **1961**, *11*, 328.

(3) Structure: Omura, S.; Matsubara, H.; Nakagawa, A.; Furusaki, A.; Matsumoto, T. J. *Antibiot. Chemother.* (*Washington, D.C.*) **1980**, *33*, 915.

(4) McGuire, J. M.; Bonieces, W. S.; Higgins, C. E.; Hoehn, M. M.; Stark, W. M.; Westhead, J.; Wolfe, R. N. *Antibiot. Chemother.* (*Washington, D.C.*) **1961**, *11*, 320.

(5) For some recent reviews on this concept see: (a) Hanessian, S.; Dixit, D. M.; Liak, T. J. *Pure Appl. Chem.* **1981**, *53*, 129. (b) Hanessian, S. *Acc. Chem. Res.* **1979**, *12*, 159. (c) Hanessian, S. *Pure Appl. Chem.* **1977**, *49*, 1201. (d) Frazer-Reid, B.; Anderson, R. C. *Fortschr. Chem. Org. Naturst.* **1980**, *39*, 1; (e) Frazer-Reid, B. *Acc. Chem. Res.* **1974**, *8*, 192.

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