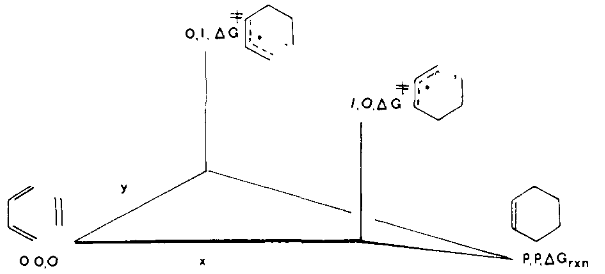
Table II. Experimental and Calculated $\Delta G^{\ddagger}$ Values and Relative Rate Constants for Cycloaddition of Dienophiles with Cyclopentadiene at 293 K

dienophile	$\Delta G^{\ddagger}{}_{xp}{}^{a}$	$\Delta G^{\ddagger}{}_{calcd}{}^{b}$	$k_{rel}{}^{xp}$	$k_{rel}{}^{calcd}$
ethylene		27.67	2.5×10^{-5} (estd)[9]	1.48×10^{-3}
acrylonitrile	24.07	23.76	1	1
fumaronitrile	21.27		78	
		20.63		184
maleonitrile	21.06		88	
1,1-dicyanoethylene	17.84	18.89	43×10^{3}	4.2×10^{3}
1,1,2-tricyanoethylene	16.37	16.6	$\sim 46 \times 10^{4}$	15×10^{4}
1,1,2,2-tetracyanoethylene	13.85	13.7	$\sim 41.4 \times 10^{6}$	19×10^{6}

[a] A. Sauer, H. Wiest, and A. Mielert, *Ber.*, **97**, 3183 (1964). [b] Calculated according to eq 1 with $\Delta G^{\ddagger}(BR_1) = \Delta G^{\ddagger}(BR_2) = 40$ kcal/mol for ethylene, $p = 1.6$, $\Delta G_{rxn} = -20$ kcal/mol and α-CN radical resonance energy = 9 kcal/m.

It is useful to examine the response of the Diels–Alder reaction of cyano-substituted dienophiles with cyclopentadiene. The appropriate nonconcerted derivatives are shown in Scheme II. While none of the thermochemical quantities have been determined experimentally, it is possible to estimate them using Benson's group additivity relations.[6] However, since only relative $\Delta G^{\ddagger}$ values shall be calculated, these values need not be estimated with more than moderate accuracy. What is important is that activation free energies of the nonconcerted alternatives will decrease by the value of the α-cyano radical resonance energy (9 kcal/mol).[7] With $p = 1.6$ the values of $\Delta G^{\ddagger}$ for all of the various cyanosubstituted dienophiles can be reproduced within 1.0 kcal/mol and the relative rates calculated to not differ by more than a factor of 2 to 10 from those observed (see Table II).

Scheme II



This model of substituent effects does not prove that the Diels–Alder reaction is concerted; other experimental work is far more persuasive in this regard,[8] but it does nicely rationalize substituent effects cited as evidence against concert.[9] However, other substituents and dienes must be pursued within this framework before general applicability can be claimed. In particular, steric effects may also play an important role, and these are currently being analyzed.[10-13]

Acknowledgments. Thanks go to the National Science Foundation for financial support and to Dr. John Bartmess, Dr. Neal Conrad, Dr. Jose Salazar, Mr. Eric Otterbacher, and Mr. J. Mike Warner for extremely helpful discussions.

References and Notes

(1) See J. J. Gajewski and N. D. Conrad, *J. Am. Chem. Soc.*, **100**, 6268, 6269 (1978), and references cited therein.

(2) For this and other examples, see S. I. Miller, *J. Am. Chem. Soc.*, **81**, 101 (1959); J. E. Critchlow, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1774 (1972); D. A. Jencks and W. P. Jencks, *J. Am. Chem. Soc.*, **99**, 7948 (1977), and references cited therein. See also note 11 of this paper.

(3) J. M. Brown, B. T. Golding, and J. J. Stufko, Jr., *J. Chem. Soc., Chem. Commun.*, 319 (1973).

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

(5) J. M. Warner, unpublished work.

(6) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

(7) W. von E. Doering, G. Horowitz, and K. Sachdev, *Tetrahedron*, **33**, 273 (1977).

(8) H. M. Frey and R. Pottinger, *J. Chem. Soc., Faraday Trans. 1*, 1827 (1979); see also J. A. Berson, P. B. Dervan, R. Malherbe, and J. A. Jenkins, *J. Am. Chem. Soc.*, **98**, 5937 (1976), and R. E. Townshend, G. Ramunni, G. Segal, W. J. Hehre, and L. Salem, *ibid.*, **98**, 2190 (1976).

(9) (a) M. J. S. Dewar, S. Olivella, and M. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 5650 (1978). (b) J. W. McIver, *Acc. Chem. Res.*, **7**, 72 (1974); *J. Am. Chem. Soc.*, **97**, 3632 (1974).

(10) Equation 1 is being applied to ionic reactions with Professor J. E. Bartmess, paper in preparation.

(11) (a) Other models for the reaction have been examined including quantum mechanical coupling, but none has reproduced the free-energy data as well as eq 1. (b) Interestingly, Professor Bartmess, using a computer model for digital solution of Lapalce's equation,[11c] has generated a surface equivalent to that generated by $Z = ax + by + cxy$. (c) R. E. Kaufman, "A Fortran Coloring Book", the MIT Press, Cambridge, Mass., 1978, pp. 255–263.

(12) (a) Equation 1 generates a "band shell" surface and provides insight into Hammett plots. In particular, the only way a Hammett plot can have a minimum is if the two coupled alternatives are near equivalent in free energy. Thus, in the substitution of benzyl bromide by radioactive bromide,[12b] the bond-breaking extreme (benzyl cation and associated particles) and the bond-making extreme (pentavalent carbon anion) must have nearly equivalent free energies! (b) S. Sugdeon and J. B. Willis, *J. Chem. Soc.*, 1360 (1951).

(13) (a) Equation 1 and the definitions leading to it allow calculation of the transition-state position. Unfortunately, the position does not correspond to the relative KIE's observed. However, the KIE's in the 3,3 shift can be reproduced by appropriate application of Miller's equation[13b] to the parallel and perpendicular coordinates[13c] of the energy surface. (b) A. R. Miller, *J. Am. Chem. Soc.*, **100**, 1984 (1978). (c) E. R. Thornton, *ibid.*, **89**, 2915 (1969).

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Charge-Transfer Luminescence from a Nonaromatic α-Diimine Complex of Ruthenium(II)

Sir:

Since the introduction of tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, as a photosensitizer,[1] there has been a surge of interest in the excited-state properties and chemistry of $[Ru(bpy)_3]^{2+}$ and related polypyridine complexes of d^6 metals.[2,3] This interest has been augmented in part by their potential utilization in solar energy conversion and in laser applications.[4,5]

To date all charge-transfer (CT) emissions from Ru(II) complexes have occurred with molecules containing aromatic bipyridines, phenanthrolines, and their isoelectronic nitrogen substituted ligand analogues.[5a,6-8] We report here proof that an aromatized cyclic ligand is not essential for CT emission. CT emissions can arise when only the α-diimine ($-N{=}C{-}C{=}N-$) functionality or at most a perturbed α-diimine is present. This result opens up a broad new class of ligands[9] for preparing potential CT emitting photosensitizers.

We have prepared the tris(2,2′-bi-2-thiazoline)ruthenium(II) complex,[10] $[Ru(bt)_3]^{2+}$, where bt has the following structure.

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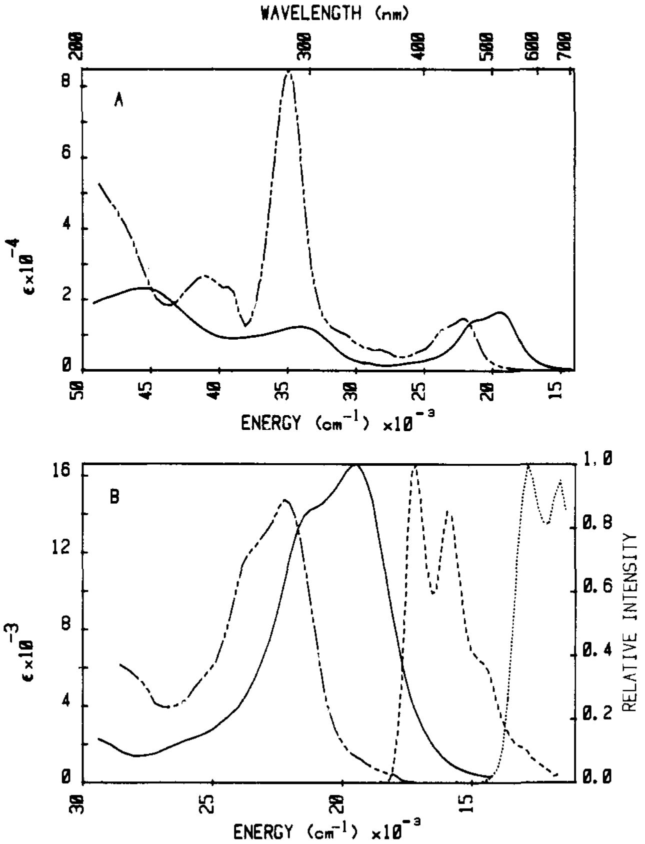
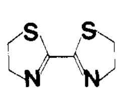


Figure 1. Room temperature absorption of $[Ru(bpy)_3]^{2+}$ (- - -) and $[Ru(bt)_3]^{2+}$ (——) in ethanol-methanol) (4:1 v/v). Corrected emission spectra of $[Ru(bpy)_3]^{2+}$ (- - -) and $[Ru(bt)_3]^{2+}$ (····) at 77 K in an ethanol-methanol (4:1 v/v) glass.



The room-temperature absorption and low-temperature emission spectra of $[Ru(bt)_3]^{2+}$ along with those for the prototype CT emitter $[Ru(bpy)_3]^{2+}$ are shown in Figure 1. $[Ru(bt)_3]^{2+}$ does not emit in solution at room temperature; at 77 K the emission is weak ($\Phi = 3 \times 10^{-4}$),[13] but is easily measurable and the decay time is 80 ns. In spite of the great skeletal differences between the bt and bpy ligands, the similarity between the two sets of spectra is striking. Except for the former complexes' bathochromic shifts in the absorption (2650 cm^{-1}) and emission (4230 cm^{-1}), the structure, band shapes and widths, and molar extinction coefficients for the two complexes are almost identical. The intense absorption of $[Ru(bt)_3]^{2+}$ at 19.42 kcm^{-1} (ϵ 16 600) is very similar to the low-lying CT bands of $[Fe(bt)_3]^{2+}$ [15] and a related series of saturated α-diimine-Fe(II) complexes.[16] The observed blue shift on going from Fe(II) and to Ru(II) complexes is characteristic of metal-to-ligand CT (MLCT) transition of polypyridine complexes. On these grounds we assign the low-energy absorption of $[Ru(bt)_3]^{2+}$ to a MLCT transition.[17]

We assign the emission of $[Ru(bt)_3]^{2+}$ to a d-π^* MLCT transition. This assignment is supported by the following considerations. The emission is at least 8 kcm^{-1} too low in energy to arise from a ligand fluorescence or phosphorescence. The sharpness and vibrational structure of the emission is characteristic of MLCT emissions,[6-8] but not of d-d emissions of d^6 complexes which are much broader and structureless at 77 K.[18] Also, we would expect bt to function as a ligand with a reasonably high crystal field strength which would raise the lowest ligand-field excited states[19] to well above the ~13-kcm^{-1} emitting level. Also, the splitting between the first emission maximum and the most intense CT absorption is ~6.4 kcm^{-1} which again is consistent with a MLCT assignment; for polypyridine-Ru(II) and -Os(II) complexes exhibiting CT emissions, these spacings are 4.5-6.5 kcm^{-1}.

Crosby and co-workers have demonstrated that spin-orbit coupling is so great in $[Ru(bpy)_3]^{2+}$ and related Ru(II) complexes, that a singlet-triplet classification of their CT states is probably meaningless.[7] For similar reasons a fluorescence or phosphorescence assignment to the emission of $[Ru(bt)_3]^{2+}$ would be meaningless, and we refer to this emission only as a luminescence from a spin-orbit CT state.

As further verification of a d-π^* CT assignment of the emission of $[Ru(bt)_3]^{2+}$, we have compared the intrinsic lifetime, τ_0, of $[Ru(bt)_3]^{2+}$ with the value estimated from the semiempirical spin-orbit coupling model[20] of Demas and Crosby which was originally used with Ru(II)-polypyridine complexes. The τ_0 from emission results was ~240 μs, while that estimated from the spin-orbit coupling model was ~60 μs. Given the simplicity of the model, the agreement is satisfactory and further emphasizes the similarity in emission character of Ru(II)-polypyridine complexes with those containing only the α-diimine chromophore.

Acknowledgment. We gratefully acknowledge support by the National Science Foundation (CHE 77-20379 and CHE 77-09296) and the Air Force Office of Scientific Research (AF0SR78-3590).

References and Notes

(1) (a) Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* **1971**, *93*, 1800-1801. (b) Gafney, H.; Adamson, A. W. *ibid.* **1972**, *94*, 8238-8239.

(2) (a) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321-433. (b) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970.

(3) (a) Jonak, G. D.; Matheson, M. S.; Meisel, D. *J. Am. Chem. Soc.* **1978**, *100*, 1449-1456. (b) Hoselton, M. A.; Lin, C.-T; Schwarz, H. A.; Sutin, H. *ibid.* **1978**, *100*, 2383-2388. (c) Winterle, J. S.; Kliger, D. S.; Hammond, G. S. *ibid.* **1976**, *98*, 3719-3721. (d) Demas, J. N.; Harris, E. W.; McBride, R. P. *ibid.* **1977**, *99*, 3547-3551.

(4) (a) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, R. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1976**, *98*, 2337-2338; **1977**, *99*, 4947-4953. (b) Lehn, J. M.; Sauvage, J. P. *Nouv J. Chim.* **1978**, *1*, 449.

(5) (a) Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536-6544. (b) Clark, W. D. K.; Sutin, N. *ibid.* **1977**, *99*, 4676-4682; (c) Lin, C.-T; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97-105.

(6) (a) Klassen, D. M.; Crosby, G. A. *J. Chem. Phys.* **1968**, *48*, 1853-1858. (b) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841-2847.

(7) (a) Harrigan, R. W.; Crosby, G. A. *J. Chem. Phys.* **1973**, *59*, 3468-3476. (b) Harrigan, R. W.; Hager, G. D.; Crosby, G. A. *Chem. Phys. Lett.* **1973**, *21*, 487-490. (c) Hager, G. D.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7031-7036. (d) Hager, G. D.; Watts, R. J.; Crosby, G. A. *ibid.* **1975**, *97*, 7037-7041. (e) Hipps, K. W.; Crosby, G. A. *ibid.* **1975**, *97*, 7042-7048.

(8) (a) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660-2666. (b) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370-7371.

(9) (a) Krumholz, P. "Structure and Bonding", Jorgensen, C. K., Ed.; Springer-Verlag: New York, 1971; Vol. 9, pp 139-174. (b) Krumholz, P.; Serra, O. A.; DePaoli, M. A. *Inorg. Chim. Acta* **1975**, *15*, 25-32.

(10) Synthesis of tris(bt)ruthenium(II). A suspension of 0.180 g (0.48 mmol) of $K_2RuCl_5 \cdot H_2O$ in 30 mL of glycerol was stirred and heated to 100 °C. The subsequent hot green solution was added to 0.312 g (1.92 mmol) of bt[11] suspended in ~5 mL of glycerol and heated at 70 °C for 1 h. The hexafluorophosphate or perchlorate salts were obtained by cooling and diluting the reaction mixture with H_2O, filtering, and adding ~5 mL of a saturated aqueous solution of ammonium hexafluorophosphate or sodium perchlorate. The deep violet precipitates were recrystallized from acetone-ethanol.

(11) The crude ligand was purified according to the method of Nelson, J.; Nelson, S. M.; Perry, W. D. *J. Chem. Soc., Dalton Trans.* **1976**, 1282-1287 and prepared by the method in a reference cited therein.

(12) Anal. Calcd for $[Ru(bt)_3](ClO_4)_2$: C, 26.47; H, 2.96; Cl, 8.68; N, 10.29; S, 23.55. Found: C, 26.38; H, 2.93; Cl, 8.64; N, 10.19; S, 23.58. Anal. Calcd for $[Ru(bt)_3](PF_6)_2$: C, 23.81; H, 2.66; N, 9.26; S, 21.19. Found: C, 24.29; H, 2.62; N, 8.89; S, 20.64. The former perchlorate salt was also judged to be analytically purer by its emission spectrum.

(13) The method of Parker and Rees[14] was used to determine the approximate absolute quantum yield at 77 K. The standard used was bis(bipyridine)-oxalatoruthenium(II) (Φ = 0.0124).[6b] To account for the emission component of the $[Ru(bt)_3]^{2+}$ complex which extended beyond the ~870-nm limit of the phototube, integrated emission intensities of the standard and $[Ru(bt)_3]^{2+}$ were compared over nearly equivalent energy bandwidths to obtain the quantum yield. Φ is estimated to be accurate to ±60%. Optical densities of the reference and unknown at the excitation wavelength 460 nm were matched at room temperature.

(14) Parker, C. A.; Rees, W. T. *Analyst* **1960**, *85*, 587-600.

(15) $[Fe(bt)_3](ClO_4)_2$ in CH_3CN has a CT band maximum at 16.8 kcm^{-1} (ϵ 12 400).[11]
(16) $[Fe(\alpha\text{-diimine})_3]^{2+}$ complexes have CT maxima ranging from 16.7 to 18.0 kcm^{-1} (ϵ 8500 to 12 400).[9b]
(17) By analogy to Krumholz' assignment[9] for the related Fe(II)-α-diimine complexes, we tentatively assign the low-energy absorption maximum at 19.42 kcm^{-1} (ϵ 16 600) and the higher energy shoulder at 21.4 kcm^{-1} to two MLCT transitions assuming a D_3 symmetry and trigonal splitting of the t_2 d orbitals and π^* orbitals. The intensity ($\epsilon > 10^4$) further supports a CT assignment. At higher energies, 32.4 and 45.9 kcm^{-1}, we have observed the intraligand π-π^* transitions (ϵ 12 900) and (ϵ 25 000), respectively. For a theoretical treatment of Ru(II)-polypyridine assignments, cf. ref 7e.
(18) (a) DeArmond, M. K. *Acc. Chem Res.* **1974,** *7*, 309–315. (b) Crosby, G. A. *ibid.* **1975,** *8*, 231–238. (c) Carsten, D. H. W.; Crosby, G. A. *J. Mol. Spectrosc.* **1970,** *34*, 113–115.
(19) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976,** *98*, 4853–4858.
(20) For this calculation the spin-orbit coupling matrix element $K|M_{so}|^2$ value of 3.78×10^{-7} (M cm)/μs of $[Ru(bpy)_3]Cl_2$ was used.[6b]

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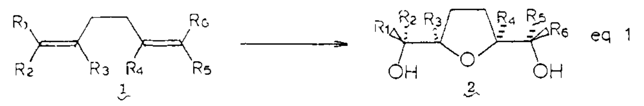
Stereochemistry of the Permanganate Oxidation of 1,5-Dienes

Sir:

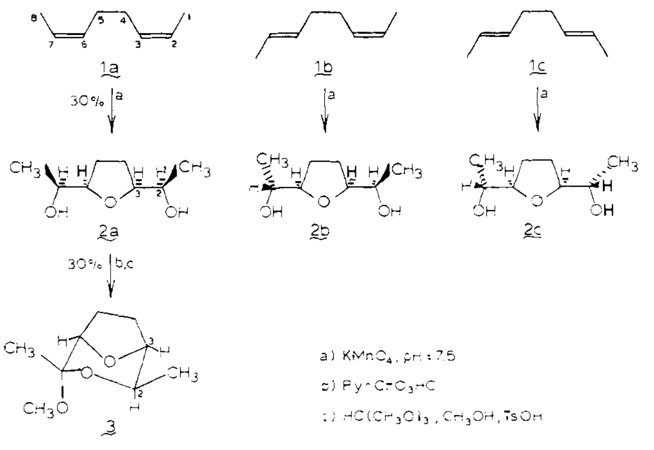
In 1965 Klein and Rojahn reported that oxidation of 1,5-dienes structurally related to geraniol and nerol (**1**, $R_1 = R_2 = R_4 = CH_3$; R_3 = H; $R_5 \neq R_6$) with potassium permanganate under slightly alkaline conditions afforded 2,5-bis(hydroxymethyl)tetrahydrofurans **2** with relative stereochemistry as shown in eq 1.[1,2] From a mechanistic viewpoint, these results are provocative, particularly in light of the recent proposals of Sharpless concerning the mechanism of oxidations of olefins by oxo transition metal species.[3] They are especially intriguing from the standpoint of synthetic chemistry in suggesting that stereocontrolled synthesis of 2,5-bis(hydroxymethyl)tetrahydrofurans **2** with *four* chiral centers ($R_1 \neq R_2$; $R_5 \neq R_6$) may be accomplished via stereoselective synthesis of the appropriate 1,5-diene precursor. To our knowledge, no report concerning permanganate oxidation of a 1,5-diene containing four unsymmetrically substituted olefinic carbons (**1**, $R_1 \neq R_2$; $R_5 \neq R_6$) has appeared in the literature, and no quantitative analytical data regarding the extent of stereospecificity of the transformation for any 1,5-diene is available for mechanistic consideration. Therefore, as part of a study on the scope and mechanism of this reaction, particularly relating to the development of methodology for stereocontrolled total synthesis of tetrahydrofuran containing natural products (e.g., monensin[4]), we describe here our work on the oxidation of the three isomeric 2,6-octadienes.



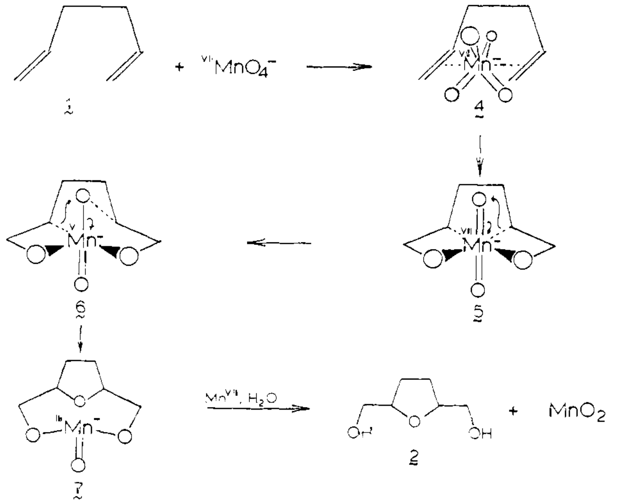
The results of our study show that diols **2a–c** (Scheme I) are indeed formed from dienes **1a–c**, respectively, with >97% stereospecificity. A mechanistic rationalization of these results is presented. Our mechanism involves Sharpless type[3] [2 + 2] insertions of the olefinic π bonds into metal oxo bonds of manganese. The key tetrahydrofuran-forming step is a reductive elimination with migration of carbon from manganese to oxygen with retention of configuration.

The known (*Z,Z*)-, (*E,Z*)-, and (*E,E*)-2,6-octadienes **1a**, **1b**, and **1c**, respectively[5] (Scheme I), were prepared stereoselectively in our laboratories from 1,5-hexadiyne. Oxidative cyclization of (*Z,Z*)-2,6-octadiene (**1a**, 2 molar equiv of $KMnO_4$, 10% aqueous acetone solvent, CO_2 ebullition, −20 °C, ½ hr) followed by filtration of MnO_2, removal of acetone and water in vacuo, and simple gravity chromatography of the residue on silica gel gave a pure diol, assigned structure **2a**,[6] albeit in a disappointingly low 32% yield. Similarly, oxidation of dienes **1b** and **1c** produced diols assigned structures **2b** and **2c**, respectively.[6] The cis-2,5-disubstituted tetrahydrofuran assignment was made based upon literature precedent[1] and upon an analysis of the product obtained from oxidation of 1,5-hexadiene. In this case the known[1,7] *cis*-2,5-bis(hydroxymethyl)tetrahydrofuran is produced with no trans diol impurity detectable by ^{13}C NMR. The structural assignments for diols **2a–c** were confirmed by single crystal X-ray analysis of the bicyclic ketal **3**,[6] prepared from diol **2a** as shown in Scheme I. This crystal structure establishes the 2*R*,3*S* configuration for diol **2a**[2] allowing an unambiguous assignment of relative stereochemistry for all three diols based upon symmetry properties readily deduced from the ^1H and ^{13}C spectra.

Scheme I



Scheme II



Gas chromatographic analysis of the purified diols **2a–c** showed very little cross contamination. For example, GC analysis of diol **2b** on an 0.2% Carbowax 20M on Chromasorb 20W column showed <0.5% diol **2c** and 2% diol **2a**. An absolute lower limit of 97% stereospecificity was set for this reaction by a careful GC analysis of the crude reaction mixture from oxidation of (*Z,Z*)-2,6-octadiene (**1a**). This analysis showed a peak with the same retention time as diol **2b**, with 3% the area of the peak corresponding to diol **2a**.

Classical ideas concerning the mechanism of the permanganate oxidation of olefins[8] offer little help in understanding this rather remarkable transformation. Though several possible modes for formation of diols **2a–c** may be envisioned, the high