(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.

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(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:

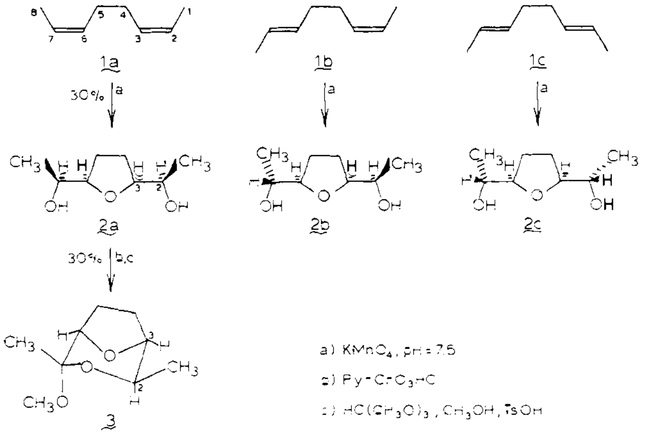
In 1965 Klein and Rojahn reported that oxidation of 1,5-dienes structurally related to geraniol and nerol (**1**, $R_1 = R_2 = R_4 = CH_3$; $R_3 = H$; $R_5 \neq R_6$) with potassium permanganate under slightly alkaline conditions afforded 2,5-bis(hydroxymethyl)tetrahydrofurans **2** with relative stereochemistry as shown in eq 1.[1,2] From a mechanistic viewpoint, these results

eq 1

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.

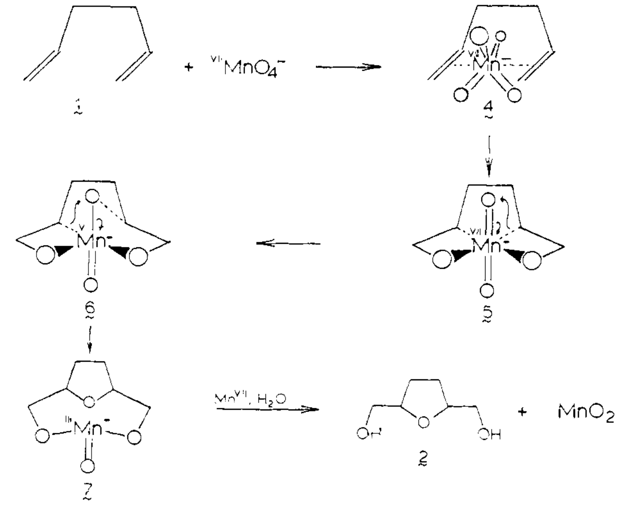
The results of our study show that diols **2a–c** (Scheme I) are indeed formed from dienes **1a–c**, respectively, with >97% stereospecificity. A mechanistic rationalization of these results is presented. Our mechanism involves Sharpless type[3] [2 + 2] insertions of the olefinic π bonds into metal oxo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

Scheme I



a) $KMnO_4$, pH = 7.5
b) Py-C-C_3H-C
c) $HC(CH_3O)_3$, CH_3OH, TsOH

Scheme II



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, 1/2 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.

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

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stereoselectivity and retention of configuration at all four olefinic centers is difficult to rationalize. Yet, application of the Sharpless proposals[3] allows a beautifully simple explanation as outlined in Scheme II.

Initial formation of the bis-π-complex **4** between diene and MnO_4^- is followed by two Sharpless type [2 + 2] additions giving the remarkably unstrained octahedral Mn(VII) intermediate **5**. Alkyl migration with retention to give **6**, followed by the key reductive elimination with retention, affords Mn(III) diester **7**. Oxidation of intermediate **7** and hydrolysis then yields MnO_2 and diol **2** with correct relative stereochemistry. Clearly, several reasonable variations of this mechanism involving differences in timing of the [2 + 2] additions, alkyl migrations, and oxidation of intermediate manganese species may be readily imagined. We feel that the crucial step involving migration of carbon from manganese to oxygen forming the THF ring with retention (**6** → **7**) elegantly explains the observed results. Indeed, we feel that the ease with which the Sharpless mechanism accounts for our results should be taken as a powerful argument in favor of Sharpless' basic proposals.

Further work on the mechanism of this reaction and its applications to the total synthesis of ionophorous natural products is in progress.

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(1) Klein, E.; Rojahn, W. *Tetrahedron* **1965,** *21*, 2353–2358.
(2) All chiral compounds discussed in this work are racemates. For the sake of clarity only the series of enantiomers in which C-3 of compounds **2a–c** (numbering as shown in Scheme I) has the *S* configuration are considered.
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(6) Diol **2a** had the following physical properties: ^1H NMR ($CHCl_3$) δ 1.13 (d, 6 H, J = 6.6 Hz, RCH_3), 1.68–2.00 (m, 4 H, RCH_2CH_2R), 3.59 (br s, 2 H, ROH), 3.86 (m, 2 H, R_2CHOR), 4.03 (q of ds, 2 H, J = 6.6, 3 Hz, R_2CHOH); ^{13}C NMR (proton decoupled, $CDCl_3$) δ 18.78, 24.12, 68.24, 83.43; IR (CCl_4) ν 3350 (s) cm^{-1}, concentration independent, OH; R_f (SiO_2, EtOAc), 0.20; bulb to bulb distillation at 75–80 °C (0.05 mm) gave analytically pure material. Anal. Calcd for $C_8H_{16}O_3$: C, 59.98, H, 10.07. Found: C, 59.92; H, 10.17. Diol **2b** had the following physical properties: ^1H NMR ($CDCl_3$) δ 1.15 (overlapping ds, 6 H, J = 6.0, 6.3 Hz, RCH_3), 1.6–2.0 (m, 4 H, RCH_2CH_2R), 3.5–4.2 (m, 6 H, R_2CHOR, OH); ^{13}C NMR (proton decoupled, $CDCl_3$) δ 18.59, 19.71, 24.32, 28.20, 67.95, 70.33, 85.78, 83.92; R_f (SiO_2, EtOAc), 0.18; purified as **2a** was. Anal. Calcd for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 59.75, H, 9.89. Diol **2c** had the following physical properties: ^1H NMR ($CDCl_3$) δ 1.16 (d, 6 H, J = 6.3 Hz, RCH_3), 1.47–2.16 (m, 4 H, RCH_2CH_2R), 3.4–3.8 (m, 6 H, R_2CHOR, ROH); ^{13}C NMR (proton decoupled, $CDCl_3$) δ 19.37, 28.10, 70.67, 84.45; IR (CCl_4) ν 3400 (s) cm^{-1}, concentration independent, OH; R_f (SiO_2, EtOAC), 0.16; purified as **2a** was. Anal. Calcd for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 59.75; H, 9.89. Ketal **3** had the following physical properties: mp 55–56 °C (vacuum); ^1H NMR ($CDCl_3$) δ 1.05 (d, 3 H, J = 6.5 Hz, R_2CHCH_3), 1.18 (s, 3 H, R_3CCH_3), 1.7–2.1 (m, 4 H, $12CH_2CH_2R$), 3.31 (s, 3 H, $ROCH_3$), 4.01 (m, 2 H, R_2CHOR), 4.13 (partially obscured q of ds, 1 H, J_{vis} = 1.8, J_{CH_3} = 6.5 Hz, $R_2CHCH(CH_3)(OR)$). Ketal **3** crystallized in space group $p2_1/n$ with a = 6.896 (2) Å, b = 15.044 (3) Å, c = 8.860 (2) Å, β = 91.62 (2)°. The structure was solved using direct methods and refined using 637 observed reflections to a residual of 0.06. A discussion of the details of the structure and spectra of this compound will appear shortly.
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(8) (a) Stewart, R. "Oxidation in Organic Chemistry, Part A", Wiberg, K. B., Ed.; Academic Press: New York, 1965; pp 1–68. (b) Wiberg, K. B.; Geer, R. D. *J. Am. Chem. Soc.* **1966,** *88*, 5827–5832. (c) Lee, D. G.; Brownridge, S. R. *ibid.* **1974,** *96*, 5517–5523.

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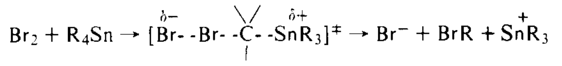
The Role of Substrate and Media Polarity on the Stereochemistries of the S_E2 Bromination of Trialkyl-*sec*-butyltin Compounds

Sir:

Although electrophilic substitution at saturated carbon has been studied in some detail,[1] little is known about the factors governing the stereochemical consequences of such reactions. The earliest stereochemical studies at carbon-tin centers examined the reaction of halogens with cyclopropyl derivatives; retention of configuration at carbon was uniformly observed,[2-5] but this was not unexpected because of the high inversion barrier.

Jensen and Davis[6] designed an organotin in accord with considerations that reaction (S_E2) by bromine might occur by an inversion process—*sec*-butyltrineopentyltin. Tetraalkyltin compounds, being coordinately saturated, would not allow a closed transition state which would force retention. The steric bulk of the neopentyl groups might serve to direct the approach of the electrophile away from the front side of the carbon-tin bond. A polar solvent, such as methanol, was utilized to support the charge-separated transition state. Indeed, the *sec*-butyltrineopentyltin was cleaved by bromine in methanol containing bromide ion to yield *sec*-butyl bromide with predominant inversion of configuration.[6,7] Although the bulk of the bromine was complexed with bromide ion to form Br_3^-, the kinetic results show conclusively that bromide ion in *any* form is *not* involved in the transition state; i.e., rate = $k[Br_2][R_4Sn]$ (eq 1, 2).

$$Br_3^- \rightleftharpoons Br_2 + Br^- \qquad (1)$$



$$Br_2 + R_4Sn \rightarrow [\overset{\delta-}{Br}{-}{-}Br{-}{-}C{-}{-}\overset{\delta+}{Sn}R_3]^{\ddagger} \rightarrow Br^- + BrR + \overset{+}{Sn}R_3 \qquad (2)$$

I

Obviously, the next experiment to perform was to carry out the bromination in carbon tetrachloride wherein the separated ionic products of eq 2, Br^- and R_3Sn^+, would be of high energy. When this was done under conditions minimizing free-radical reactions, retention of configuration was observed.[8,9]

Recently, Rahm and Pereyre have criticized the stereochemical result in methanol claiming that retention, in the absence of front-side steric hindrance, is *general* for electrophilic substitution of *sec*-butyltrialkyltin compounds.[10] In support of this contention, these workers reported that *sec*-butyltriisopropyltin is brominated in methanol–cyclohexane with 45% retention of configuration. However, this result is not directly comparable with that of Jensen and Davis, since both the solvent system and structure of the organotin were changed.

In this report it is shown that the choice of leaving group (R_3Sn^+, eq 2) and of solvent can *independently* govern the stereochemical consequence of electrophilic substitution reactions of secondary alkyltin compounds. The only reasonable conclusion is that there is *no* preferred stereochemistry for this reaction and a delicate energy difference exists between inversion and retention pathways.

The steric bulk of the organotin compounds was varied, utilizing the four organotins *sec*-butyl(neopentyl)$_n$(isopropyl)$_{3-n}$. The requisite compounds were obtained from *sec*-butyltriphenyltin[11] of known optical purity and configuration.[12,13] The stereochemical results of the bromination of the four organotins in carbon tetrachloride, methanol (with and without added sodium bromide), and acetonitrile solvent systems are presented in Table I.

In carbon tetrachloride, in the presence of a free-radical inhibitor, a high degree of retention is uniformly observed, irrespective of the bulk of the R_3Sn- group. With methanol

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