

2-10, the rate laws for both reactions (eq 6 and 7) include both pH-dependent and pH-independent terms. Rate constants for the separate pathways have been obtained from kinetics data obtained by using stopped-flow or simple mixing techniques over the pH range 2-10.

$$-d[(bpy)_2(py)RuO^{2+}]/dt = [H_2O_2][(bpy)_2(py)RuO^{2+}](k_1^{IV} + k_2^{IV}[H^+]^{-1}) \quad (6)$$

$$k_1^{IV}(I = 0.1, 25^\circ C) = 2.10 \pm 0.07 M^{-1} s^{-1}$$

$$k_2^{IV}(I = 0.1, 25^\circ C) = (6.03 \pm 0.35) \times 10^{-8} s^{-1}$$

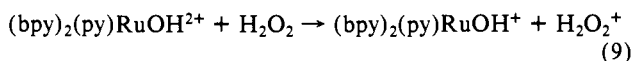
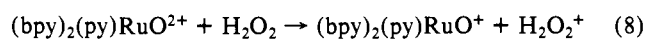
$$-d[(bpy)_2(py)RuOH^{2+}]/dt = [H_2O_2][(bpy)_2(py)RuOH^{2+}](k_1^{III} + k_2^{III}[H^+]^{-1}) \quad (7)$$

$$k_1^{III}(I = 0.1, 25^\circ C) = (5.44 \pm 0.06) \times 10^{-2} M^{-1} s^{-1}$$

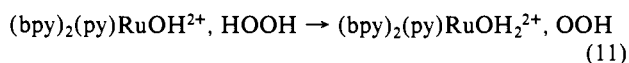
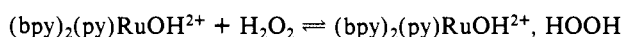
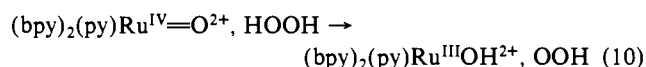
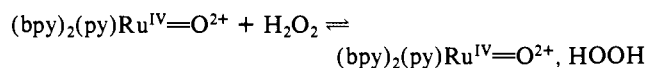
$$k_2^{III}(I = 0.1, 25^\circ C) = (6.55 \pm 0.15) \times 10^{-9} s^{-1}$$

The oxidations involving Ru(III) must proceed via an initial one-electron step, whereas the Ru(IV) oxidations could proceed, at least in principle, via one- or two-electron steps.<sup>1,3</sup> We have been able to demonstrate that the Ru(IV) reactions also involve initial one-electron steps by stopped-flow spectrophotometry. A two-electron mechanism would necessarily involve the formation of  $(bpy)_2(py)RuOH_2^{2+}$  as the initial product. However, because of the comproportionation in eq 1, the Ru(II) complex can only be observed as product at high concentrations of  $H_2O_2$  where the rate of oxidation of  $H_2O_2$  exceeds the rate of comproportionation. We find that under the appropriate conditions ( $[H_2O_2] = 0.4 M$ ,  $[Ru^{IV}] = 2.5 \times 10^{-5} M$ ) the initial product of the reaction is  $(bpy)_2(py)Ru^{III}OH^{2+}$ .

The most striking observation in our work is that the acid-independent pathways in  $D_2O$  as solvent show the existence of H-D isotope effects of a considerable magnitude: for  $(bpy)_2(py)RuO^{2+}$  at 25 °C,  $k_{H_2O}/k_{D_2O} = 22.1 \pm 0.6$ ; for  $(bpy)_2(py)RuOH^{2+}$ ,  $k_{H_2O}/k_{D_2O} = 16.7 \pm 0.5$ . The existence of such dramatic effects is reminiscent of the comproportionation reaction in eq 1. The origin of the effect is probably closely related and is no doubt reflective of a similarity in mechanisms. As shown in eq 8 and 9, simple outer-sphere electron transfer would result in initial

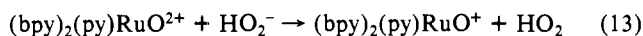
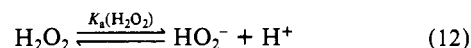


products having nonequilibrium high-energy structures with regard to proton content. On the other hand, as shown in eq 10 and 11,



proton-coupled electron transfer would result in the appropriate proton composition in the products, but at the cost of a more complex mechanism. In the coupled mechanism, strong electronic interactions may exist between the  $Ru^{IV}O$  group and the OH group of  $H_2O_2$ , or if electronic coupling is weak, a long-range proton tunneling must occur between redox sites. As yet, the detailed nature of the proton-electron transfer is unclear and may involve, in part, solvent O-H (or O-D) bonds.

The isotope effect data for the inverse acid path support the importance of proton content in determining the redox mechanism. The most straightforward interpretation of the proton dependence is that the pathways involve the oxidation of  $HO_2^-$ , as shown in eq 12 and 13, with  $(bpy)_2(py)RuO^{2+}$  as oxidant. With this in-



terpretation,  $k_2^{III}$  and  $k_2^{IV}$  are the product of the acid dissociation constant for  $H_2O_2$ ,  $K_a(H_2O_2)$ ,<sup>4</sup> and the rate constant for  $HO_2^-$  oxidation ( $k_2^{III}(\text{redox})$  and  $k_2^{IV}(\text{redox})$ ). With the value of  $K_a(H_2O_2) = 2.28 \times 10^{-12}$  at 25 °C and  $I = 0.1 M$ ,  $k_2^{III}(\text{redox}) = (2.64 \pm 0.16) \times 10^4 M^{-1} s^{-1}$  and  $k_2^{IV}(\text{redox}) = (2.87 \pm 0.65) \times 10^3 M^{-1} s^{-1}$ . Although the H-D isotope effect for  $k_2^{IV}(\text{redox})$  is large,  $k_{H_2O/D_2O} = 9.91$ , a considerable fraction of the effect is no doubt from the acid-base preequilibrium for  $H_2O_2$  (note that  $K_a(H_2O)/K_a(D_2O) = 7.28$ ),<sup>5</sup> and the reactions with  $HO_2^-$  may be outer-sphere, giving  $HO_2$  directly as shown in eq 13.

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**Registry No.**  $D_2$ , 7782-39-0;  $H_2O_2$ , 7722-84-1;  $(bpy)_2(py)Ru^{III}OH^{2+}$ , 75495-07-7;  $(bpy)_2(py)Ru^{IV}O^{2+}$ , 67202-43-1.

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### Longer-Range Chiroptical Effects in Conjugated Cisoid Dienes: Contributions by Homoallylic and Bis-Homoallylic Alkyl Groups<sup>1</sup>

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Although contributions by allylic substituents to the lowest-energy Cotton effects (CEs) of chiral conjugated cisoid dienes in relation to the helicity of the diene have generated considerable interest and debate,<sup>2</sup> chiroptical effects of more remote groups have received only scant attention. In investigating this question, we have found significant CE influences by homoallylic ( $\beta$ ) and bis-homoallylic ( $\gamma$ ) methyl groups in a pertinent series of *trans*- $\Delta^{1,3}$ -hexalins.

Overall, we find that when the group is axial and close enough to one of the double bonds for a through-space interaction with the  $\pi$  or  $\pi^*$  orbital,<sup>3</sup> it makes an overriding contribution to the CE with the same sign as the helicity of the diene. When it is equatorial and lies in a coplanar "W" path to one end of the diene, it transmits an opposite, weaker effect, apparently by a through-bond mechanism.<sup>4</sup> Formally equivalent results in terms of either a *P* (right handed) or *M* (left handed) diene helicity are obtained from a multisector interpretation (Figure 1) derived by simultaneous application of the Scott-Wrixon olefin octant rule<sup>5</sup> to both double bonds.

Significantly, both approaches anticipate the CE reversal encountered in *trans*- $\Delta^{1,3}$ -hexalins when axial allylic alkyl (methyl) groups are replaced by hydrogen.<sup>2</sup> The resulting CE is opposite in sign to the helicity of the diene and is governed by chirality contributions of substituents or bonds lying between the lateral planes of the two double bonds.

(1) Presented in part at the 17th Midwest Regional Meeting of the American Chemical Society, Columbia, MO, Nov 5-6, 1981; paper no. 646; also at the 184th National ACS Meeting, Kansas City, MO, Sept 12-17, 1982; ORGN 160.

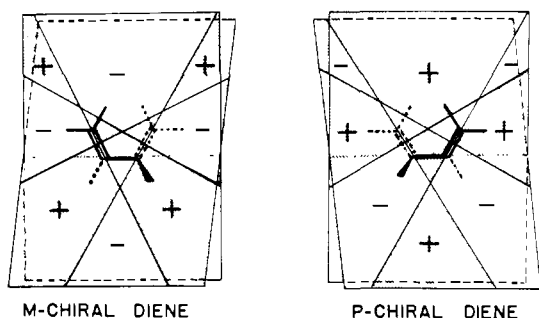
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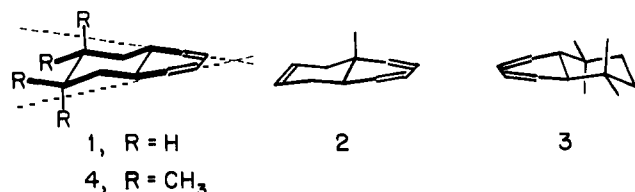


**Figure 1.** Multisector chirality rule for nonplanar conjugated cisoid dienes viewed along the edges of the planes perpendicular to each double bond. The signs are for the regions above and below the lateral planes of both double bonds; for intervening sectors the signs are opposite those shown.

A distinctive feature of the sector approach is that the chirality contribution of an axial homoallylic alkyl group has the same sign as that of an axial allylic substituent located in the same sector region. As an initial test of this prediction, we prepared<sup>6</sup> 6 $\beta$ -methyl-5 $\alpha$ -cholesta-1,3-diene<sup>7a</sup> and its 6 $\alpha$ -methyl isomer<sup>7b</sup> and compared their CEs.

In agreement with Figure 1 for an *M*-chiral diene having an axial homoallylic substituent, the 6 $\beta$ -methyl isomer has a CE that is appreciably more negative ( $\Delta\epsilon_{259} = -5.5$ )<sup>8</sup> than that of the equatorial 6 $\alpha$ -methyl isomer ( $\Delta\epsilon_{260} = -1.4$ ). The latter, with the 6 $\alpha$ -methyl group lying in a coplanar W path to C-1, has a CE that is even a little less negative than that of the parent 5 $\alpha$ -cholesta-1,3-diene ( $\Delta\epsilon_{260} = -2.2$ ).<sup>9</sup> These differences persist at low temperature, indicating little conformational mobility around the chromophore.<sup>10</sup>

To gain a better understanding of the alkyl-substituent origin of these effects, we synthesized<sup>6</sup> the model (-)-*trans*- $\Delta^{1,3}$ -hexalin



(6) All key intermediates and final products were obtained in satisfactory yield and gave correct combustion analyses as well as consistent MS, IR, and NMR spectra.

(7) (a) This diene (mp 57–58 °C;  $\epsilon_{260}^{\text{hex}}$  3720) was prepared by the action of *n*-BuLi<sup>2</sup> on the tosylhydrazone of 6 $\beta$ -methyl-5 $\alpha$ -cholest-1-en-3-one, in turn obtained by the PhSeCl–H<sub>2</sub>O<sub>2</sub> procedure from the corresponding saturated ketone.<sup>4</sup> (b) This diene (mp 74–75 °C;  $\epsilon_{262}^{\text{hex}}$  3550) was similarly prepared from 6 $\alpha$ -methyl-5 $\alpha$ -cholestan-3-one.<sup>4</sup>

(8) Circular dichroism measurements were made in hexane at 20 °C or (in the low-temperature runs) methylcyclohexane–isopentane (1:3 v/v). Cryostat system: Burgstahler, A. W.; Weigel, L. O. *Lab. Pract.* **1975**, *24*, 812–813. Solvent contraction: Korver, O.; Bosma, J. *Anal. Chem.* **1971**, *43*, 1119–1120.

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(11) Dienes 1 ( $\epsilon_{260}^{\text{hex}}$  3725) and 4 ( $\epsilon_{260}^{\text{hex}}$  3775) were prepared by bis-dehydrobromination of the corresponding (-)-*trans*- $\Delta^2$ -octalin dibromides synthesized via KHSO<sub>4</sub> dehydration of the enantiomerically pure (+)-*trans*- $\beta$ -decalols (cf.: Dauben, W. G.; Olsen, E. G. *J. Org. Chem.* **1980**, *45*, 3377–3382. Leroux, H. *Ann. Chim. Phys.* **1910**, *Ser. 8*, *21*, 458–459. Fernandez, F.; Kirk, D. N.; Scopes, M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 18–21. Starting tetralone for synthesis of the tetramethyldecalol via dimethylation and sequential Li/NH<sub>3</sub>–EtOH reduction: Lednicer, D.; Emmert, D. H.; Chidester, C. G.; Duchamp, D. *J. Org. Chem.* **1971**, *36*, 3260–3266).

(12) Diene 3 ( $\epsilon_{260}^{\text{hex}}$  3480) was prepared by the PhSeCl–H<sub>2</sub>O<sub>2</sub>–tosylhydrazone route<sup>7</sup> from the corresponding (+)-tetramethyl-*trans*-2-decalone ( $\Delta\epsilon_{295}^{\text{hex}} = +1.07$ ) obtained by oxidation of the (+)-*trans*- $\beta$ -decalol derived from 3 $\beta$ -acetoxyetienic ester resolution of the Li/NH<sub>3</sub>–EtOH reduction product of 5,5,8,8-tetramethyl- $\Delta^{1(9)}$ -2-octalone (Dauben, W. G.; Rabinowitz, J.; Vietmeyer, N. D.; Wendschuh, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 4285–4292).

(1)<sup>11</sup> and the tetramethyl derivatives 3<sup>12</sup> and 4.<sup>11</sup> As anticipated, although 1 is a *P*-chiral diene, its CE is negative ( $\Delta\epsilon_{260} = -2.4$ ) and remains so on cooling ( $\Delta\epsilon_{265} = -1.6$  at 113 K). On the other hand, the *P*-chiral Tetralin 2,<sup>13</sup> having an axial allylic methyl group, exhibits the expected positive CE ( $\Delta\epsilon_{259} = +7.55$ ).<sup>2</sup>

Interestingly, the *M*-chiral diene 3 displays a weak positive CE ( $\Delta\epsilon_{267} = +0.8$  at 293 K), which, however, becomes negative on cooling ( $\Delta\epsilon_{249} = -3.5$  at 104 K). This behavior suggests that, at ordinary temperatures, a significant fraction of 3 exists with the cyclohexane ring in the flexible twist-boat conformation.<sup>10</sup> But, with cooling, the population of the chair conformation increases sufficiently to allow control of the CE by the negative chirality contributions of the two axial homoallylic methyl groups.

In the *P*-chiral diene 4, as in 1, the chair cyclohexane conformation strongly predominates,<sup>10</sup> as evidenced by the small change in the CE of 4 on cooling ( $\Delta\epsilon_{260} = -3.3$  at 293 K; ( $\Delta\epsilon_{260} = -2.6$  at 104 K). Here, the two axial  $\gamma$ -methyl groups are too far from the  $\pi$  or  $\pi^*$  orbitals—or too close to the lateral sector planes (dashed lines in 4)—to have any appreciable through-space (positive) chirality contribution. On the other hand, the two equatorial  $\gamma$ -methyl groups are aligned (bold lines) for a through-bond coplanar W transmission of the observed negative CE enhancement in 4 as compared to 1.

Although competing chirality contributions in more complex structures can obviously lead to ambiguities, especially when conformational mobility is involved, the present results clearly demonstrate the existence of interpretable longer-range chiroptical effects of alkyl substituents in homoannular dienes. Further investigations are in progress.

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### Preservation of Chirality in the Photochemical Interconversion of *trans*- $\Delta^{1,3}$ -Hexalin and *trans,cis,trans*-Cyclodeca-1,3,5-triene<sup>1</sup>

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Although the reversible conrotatory photoisomerization of asymmetrically substituted *trans*- $\Delta^{1,3}$ -hexalins to chiral *trans,cis,trans*-cyclodeca-1,3,5-trienes is known to be stereospecific,<sup>2,3</sup> the configurational stability of the inherently dissymmetric triene in unbiased systems has been a matter of conjecture.<sup>3</sup> In the case of a steroidal 5 $\alpha$ -methyl-1,3-diene, the resulting substituted cyclodecatriene exhibits configurational inversion both during the photoisomerization and also during or before competitive thermal disrotatory ring closure to the isomeric A/B cis-fused, 1,3-dienes.<sup>4</sup> On the other hand, the 1-methyl- and especially the 1,6-di-unsubstituted *trans,cis,trans*-cyclodeca-1,3,5-trienes have sufficient conformational mobility to undergo facile thermal closure to the *cis*- $\Delta^{1,3}$ -hexalins, even at ambient temperature, that the question of their retention or loss of chiral integrity during photointer-

(1) Presented at the 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 12–17, 1982; ORGN 139.

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