The resultant trifluoroacetate (mp 125–128 °C) was treated with 1 equiv of NaOH, followed by Amberlite CG-50 (H^+ form, elution with H_2O) to give **3**[21] as white crystals; mp 213 °C (dec) (lit. mp 217 °C, dec);[3b] $[\alpha]^{25}_{\mathrm{D}}$ −111° (*c* 0.2, H_2O) (lit. $[\alpha]^{25}_{\mathrm{D}}$ −109.7°).[3b] Synthetic **3** was identical in all respects (paper chromatography and IR, 360 MHz ^{1}H NMR, ^{13}C NMR) with natural domoic acid (**3**).

Acknowledgment. We thank Professor Koji Nakanishi, Director, for discussions. We are grateful to Professor Tsunematsu Takemoto and Dr. Kyosuke Nomoto for a generous gift of natural domoic acid and discussions during the initial stage of this study.

Registry No. 3, 14277-97-5; **4**, 53100-44-0; **5**, 81658-25-5; **6**, 81658-26-6; **7**, 81658-27-7; 8, 81671-20-7; **9a**, 81658-29-9; **9b**, 81802-29-1; **10**, 81802-30-4; **11**, 81658-31-3; **12**, 81658-32-4; **13**, isomer 1, 81802-31-5; **13**, isomer 2, 81658-33-5; **15**, 81658-35-7; **16**, 81658-45-9; **17**, 81658-36-8; **18**, 81658-46-0; **19**, 81658-47-1; **20**, 81658-39-1; **21**, 81703-61-9; **22**, 81658-40-4; **23**, 81703-62-0; **24**, 81703-63-1; **25**, 81658-41-5; (*R*)-i, 81802-32-6; (*S*)-i, 81802-33-7; ii, 81845-33-2; *trans*-2-(trimethylsilyl)oxy-1,3-pentadiene, 81802-34-8; 2-methyl-2-ethyl-1,3-dioxolane, 126-39-6; (*R*)-3-*tert*-butoxy-2-methyl-1-bromopropane, 60782-65-2; (*S*)-3-*tert*-butoxy-2-methyl-1-bromopropane, 59965-13-8.

---

(21) Domoic acid (**3**): ^{1}H NMR (360 MHz, D_2O) δ 6.35 (dd, $J = 11.0$, 14.9 Hz, 3′-H), 6.13 (d, $J = 11.0$ Hz, 2′-H), 5.78 (dd, $J = 7.9$, 14.9 Hz, 4′-H), 3.98 (d, $J = 8.1$ Hz, 2-H), 3.83 (q, $J = 7.6$ Hz, 4-H), 3.70 (dd, $J = 7.6$, 12.3 Hz, 5α-H or 5β-H), 3.49 (dd, $J = 7.6$, 12.3 Hz, 5β-H or 5α-H), 3.29 (dq, $J = 7.0$, 7.9 Hz, 5′-H), 3.05 (dddd, $J = 5.8$, 7.6, 8.1, 9.1 Hz, 3-H), 2.75 (dd, $J = 5.8$, 16.8 Hz, 3-CH_2CO$_2$H), 2.50 (dd, $J = 9.1$, 16.8 Hz, 3-CH_2CO$_2$H), 1.81 (s, 1′-CH$_3$), 1.27 (d, $J = 7.0$ Hz, 5′-CH$_3$).

Calculated Triplet State Energies of Carbonylheme Complexes: Relevance to Photodissociation and Postulated Paramagnetic Component

Ahmad Waleh* and Gilda H. Loew*

Molecular Theory Laboratory, The Rockefeller University
701 Welch Road, Palo Alto, California 94304

Received November 5, 1981

The possibility of low-lying paramagnetic states in iron–ligand complexes in ferrous hemoglobins, advanced by recent magnetic susceptibility measurements of Cerdonio and co-workers,[1–4] has attracted considerable attention.[5–11] In spite of an early controversy[5–7] due to the long-held view of its diamagnetic state,[12] the existence of a paramagnetic component in oxyhemoglobin[1] (HbO_2) has now been substantiated not only by the room-temperature measurements of magnetic susceptibility[2] but also by the interpretation of the temperature dependence of Mössbauer quadrupole splitting data[8] and of single-crystal Mössbauer studies.[11] Consistently, theoretical studies of an oxyheme complex[10] also predict a low-lying triplet excited state that can be in thermal equilibrium with the singlet ground state. On the other hand, the most recent report of paramagnetism in carp (carbon monoxy)-hemoglobin[3] (HbCO) is more equivocal, in view of the observed diamagnetic state of frozen human HbCO[1,12] and the small quadrupole splitting in Mössbauer resonance spectra,[13,14] both consistent with the calculated isotropic charge distribution in a singlet ferrous ($t_{2g}{}^6$, $S = 0$) state.[15] It is, therefore, important to investigate the low-energy triplet states of HbCO in order to determine whether a thermally populated paramagnetic state can be accommodated as has been suggested.[3,4]

Characterization of the triplet states of HbCO is equally important to address the unresolved questions with regard to the role of the triplet states in the process of CO photodissociation. Very recently, Stanford and Hoffman[16] have used triplet sensitization experiments to show that triplet excitation transfer to state(s) of higher than singlet multiplicity in carbonylferroporphyrin gives rise to CO dissociation. They have established an upper limit of 14 300 cm^{-1} for the energies of these states and have argued that dissociation might occur directly from the $\pi \rightarrow \pi^*$ configurations.[17] In recent studies,[18,19] however, we have shown that the singlet $d_\pi \rightarrow d_{z^2}{}^*$ states rather than $\pi \rightarrow \pi^*$ states are photodissociating and that the intersystem crossing to low-energy triplet states is not necessary for initiating dissociation but may occur as one of the early events of the photodissociation process.

In this communication, we report the results of calculations of the energy and nature of the low-energy triplet states of model carbonylheme complexes consisting of a hexacoordinated ferrous–porphyrin system with CO and imidazole axial ligands for four different iron–ligand geometries: one linear ($\alpha = 0°$, $\beta = 180°$) as in model compounds[20,21] and three nonlinear, tilted ($\alpha = 14°$, $\beta = 180°$), bent ($\alpha = 0°$, $\beta = 135°$), and kinked ($\alpha = 7°$, $\beta = 162°$) representing intact hemoproteins,[22–27] where α is the angle C–Fe–heme normal and β is the Fe–C–O bond angle. The three nonlinear geometries chosen are consistent with the known position of the oxygen atom from neutron and X-ray diffraction studies and reflect the uncertainty in the carbon atom position in intact hemoproteins. The details of the complete geometries including those of porphyrin and imidazole ligand are given elsewhere.[15] The linear geometry calculations were also repeated with the iron–imidazole system 0.24 Å from the center of the porphyrin plane with and without a corresponding displacement of CO ligand. The calculations were carried out by using an INDO-SCF-MO-LCAO-CI program[28–32] using an INDO/1 ap-

---

(1) Cerdonio, M.; Congiu-Castellano, A.; Mogno, F.; Pispisa, B.; Romani, G. L.; Vitale, S. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 398–400.

(2) Cerdonio, M.; Congiu-Castellano, A.; Calabrese, L.; Morante, S.; Pispisa, B.; Vitale, S. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 4916–4919.

(3) Cerdonio, M.; Morante, S.; Vitale, S.; De Young, A.; Noble, R. W. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 1462–1465.

(4) Cerdonio, M.; Morante, S.; Vitale, S. *Isr. J. Chem.* **1981**, *21*, 76–80.

(5) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 2612–2613.

(6) (a) Huynh, B. H.; Case, D. A.; Karplus, M. *J. Am. Chem. Soc.* **1977**, *99*, 6103–6105. (b) Case, D. A.; Huynh, B. H.; Karplus, M. *Ibid.* **1979**, *101*, 4433–4453.

(7) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 265–272.

(8) Bacci, M.; Cerdonio, M.; Vitale, S. *Biophys. Chem.* **1979**, *10*, 113–117.

(9) Drago, R. S.; Corden, B. B. *Acc. Chem. Res.* **1980**, *13*, 353–360.

(10) Herman, Z. S.; Loew, G. H. *J. Am. Chem. Soc.* **1980**, *102*, 1815–1821.

(11) Maeda, Y.; Harami, T.; Morita, Y.; Trautwein, A.; Gonser, U. *J. Chem. Phys.* **1981**, *75*, 36–43.

(12) Pauling, L.; Coryell, C. D. *Proc. Natl. Acad. Sci. U.S.A.* **1936**, *22*, 210–216.

(13) Marcolin, H. E.; Reschke, R.; Trautwein, A. *Eur. J. Biochem.* **1979**, *96*, 119–123.

(14) Maeda, Y.; Harami, T.; Morita, Y.; Trautwein, A.; Gonser, U. *J. Phys.* **1979**, *40*, Colloque C2, C2-500–C2-501.

(15) Herman, Z. S.; Loew, G. H.; Rohmer, M.-M. *Int. J. Quantum Chem., Quantum Biol. Symp.* **1980**, *7*, 137–153.

(16) Stanford, M. A.; Hoffman, B. M. *J. Am. Chem. Soc.* **1981**, *103*, 4104–4113.

(17) Hoffman, B. M.; Gibson, Q. H. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 21–25.

(18) Waleh, A.; Loew, G. H. *J. Am. Chem. Soc.* **1982**, *104*, 2346–2351.

(19) Waleh, A.; Loew, G. H. *J. Am. Chem. Soc.* **1982**, *104*, 2352–2356.

(20) Hoard, J. L. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 351–371.

(21) Peng, S. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8032–8036.

(22) Huber, R.; Epp, O.; Formanek, H. *J. Mol. Biol.* **1970**, *52*, 349–354.

(23) Norvell, J. C.; Nunes, A. C.; Schoenborn, B. P. *Science (Washington, D.C.)* **1975**, *190*, 568–570.

(24) Padlan, E. A.; Love, W. E. *J. Biol. Chem.* **1975**, *249*, 4067–4078.

(25) Heidner, E. J.; Ladner, R. C.; Perutz, M. F. *J. Mol. Biol.* **1976**, *104*, 707–722.

(26) Tucker, P. W.; Phillips, S. E. V.; Perutz, M. F.; Houtchens, R.; Caughey, W. S. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1076–1080.

(27) Baldwin, J. M. *J. Mol. Biol.* **1980**, *136*, 103–128.

(28) Ridley, J.; Zerner, M. *Theor. Chim. Acta (Berlin)* **1973**, *32*, 111–134.

(29) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta (Berlin)* **1976**, *42*, 223–236.

(30) Bacon, A. D. Ph. D. Dissertation, University of Guelph, Guelph, Canada, 1976.

(31) Bacon, A. D.; Zerner, M. C. *Theor. Chim Acta* **1979**, *53*, 21–54.

0002-7863/82/1504-3513$01.25/0

Table I. Triple State Energies of Carbonylheme Complexes for Different Fe–C–O Geometries (cm^{-1})[a]

Fe in plane				Fe out of plane		
bent (Fe–C = 1.77 Å)	kinked (Fe–C = 1.77 Å)	tilted (Fe–C = 1.77 Å)	linear (Fe–C = 1.77 Å)	linear (Fe–C = 1.77 Å)	linear (Fe–C = 2.01 Å)	major transition[b] component
11 191	11 178	11 178	11 187	10 909	10 979	a_{1u}; $a_{2u} \rightarrow e_g^*$
11 228	11 208	11 216	11 210	10 923	10 992	
11 681						$(d_\pi, e_g) \rightarrow d_{z^2}^*$
13 094						
13 971	13 946	13 867	13 850	13 382	13 649	a_{1u}; $a_{2u} \rightarrow e_g^*$
14 039	14 012	13 924	13 911	13 428	13 702	
15 588						$d_{x^2-y^2} \rightarrow d_{z^2}^*$
					17 076	$(d_\pi, e_g) \rightarrow d_{z^2}^*$
					17 262	
18 671	18 898	18 910	18 851	17 480	18 023	$d_{x^2-y^2} \rightarrow d_{xy}$
20 133	19 405[c]	19 042	19 656	18 671	18 795	$(d_\pi, e_g) \rightarrow e_g^*$
20 857	20 273	20 013	20 669	19 421	19 581	
21 426	20 370	20 221	20 889	19 778	19 870	
21 607	20 997	20 474	21 023	19 995	19 958	
	21 638					
	21 766					
		22 077[d]	22 120[d]	20 324[d]		$(d_\pi, e_g) \rightarrow d_{z^2}^*$
		23 379	22 239	20 551		
		(30%)	(40%)	(14%)		

[a] The states are given in the order of their energies for all geometries, and the spacing between successive states is to provide visual alignment of the states which were insensitive to changes in the ligand geometry. [b] All symmetry designations refer to porphyrin π orbitals in D_{4h} symmetry. In the coordinate system chosen, the pyrrole nitrogen atoms bisect the xy axes, and therefore, the d_{xy} orbital becomes the "e_g" partner of d_{z^2}. Multiple transitions of the same type reflect degeneracy of the molecular orbitals involved. [c] Mixture of $(d_\pi, e_g) \rightarrow d_{z^2}^*$ and $(d_\pi, e_g) \rightarrow e_g^*$ transitions. [d] Lowest energy triplet states with significant $(d_\pi, e_g) \rightarrow d_{z^2}^*$ contributions, shown in parentheses. Other states with contributions from $(d_\pi, e_g) \rightarrow d_{z^2}^*$ transition occur at higher energies.

proximation with the two-center repulsion integrals evaluated by an empirical Weiss–Mataga–Nishimoto formula.[33,34] Triplet state energies were calculated with 196 single excitation configurations corresponding to excitations from 14 highest occupied orbitals into 14 lowest virtual orbitals.

Table I shows the calculated low-energy triplet states for each of the Fe–C–O geometries investigated. The states are in numerical order and aligned to emphasize the effect of ligand geometry change. The major contribution to the excitation for each group of states are also given in terms of the main atomic orbitals in the filled and virtual molecular orbitals. The cutoff energy, in Table I, is chosen such that, at least, the lowest energy triplet states with significant contribution from $d_\pi \rightarrow d_{z^2}^*$ transitions are included for all geometries.

The essential features of the results are as follows. The lowest energy triplet states in all cases correspond to $\pi \rightarrow \pi^*$ transitions of the Q-band with an energy on the order of about 11 000 cm^{-1} above the reference ground state. The states corresponding to $d_\pi \rightarrow d_{z^2}^*$ and $d_{x^2-y^2} \rightarrow d_{z^2}^*$ transitions are most sensitive to ligand geometry. In the bent CO complex, the $^3(d_\pi \rightarrow d_{z^2}^*)$ states, which are in the same energy range as the $^3(\pi \rightarrow \pi^*)$ states, are about 10 000 cm^{-1} lower in energy than the corresponding states in the linear CO complex. By comparison, the same states, in the kinked geometry, are only about 3000 cm^{-1} lower and, in the tilted geometry, are slightly higher in energy than those in the linear geometry. Inspection of the characters of the states of higher energy (not shown in Table I) shows that the tilted CO geometry actually tends to stabilize the $d_\pi \rightarrow d_{xy}^*$ transitions relative to $d_\pi \rightarrow d_{z^2}^*$ transitions. The calculated lower energy of the $^3(d_\pi \rightarrow d_{z^2}^*)$ state with iron out of the porphyrin plane and Fe–C = 2.01 Å is due to the iron–carbon bond lengthening and is related to the dissociative nature of this state.[18] The motion of the iron out of the porphyrin plane, otherwise, does not affect the results significantly.

The calculated energy separation of 11 000 cm^{-1} between the lowest energy triplet state and the reference ground state of HbCO is independent of the Fe–C–O geometry and is much too high to accommodate a thermally populated paramagnetic state in HbCO. Moreover, this value, obtained at single CI level, is a lower limit and inclusion of appropriate double CI should increase the energy difference even further. These results argue convincingly against the assumption of the existence of a paramagnetic component in HbCO.[3,4]

HbCO and HbO_2 are rather dissimilar in this respect, and the paramagnetism of HbO_2 is related to the subtle differences between the two exchangeable ligands. The origin of the paramagnetism in HbO_2[1,2,10] is the strong mixing of the d_{yz} iron orbital and π_g oxygen orbitals, giving rise to a $(O\pi_g, d_{yz})^*$ molecular orbital as the lowest energy virtual orbital in the oxyheme complex.[10,19] By contrast, d_π and CO_π orbitals do not mix strongly in carbonylheme complex, and the $(CO\pi, d_\pi)^*$ virtual orbitals are at higher energies than e_g^*.[18] Not only does this difference lead to much higher energy triplet states in HbCO complexes than in HbO_2 complexes, but we have shown previously[19] that the same difference also results in an additional photodissociation channel for HbO_2 that does not exist in HbCO and accounts for the differences in their photodissociation properties.

The calculated lower limit (single CI) of the lowest energy $^3(\pi \rightarrow \pi^*)$ states for all geometries and the $^3(d_\pi \rightarrow d_{z^2}^*)$ state for the bent CO geometry are in very good agreement with the experimental upper limit estimate of a triplet state of 14 300 cm^{-1}.[16] Inclusion of double CI will probably improve this agreement, since the largest contribution to the depression of the ground state of carbonylheme complexes seems to arise from the configurations involving a_{1u}, a_{2u}, and e_g^* molecular orbitals and is estimated to be on the order of 3000 cm^{-1}.[35] Strictly speaking, the experimental results[16] should be compared with those for the linear CO, in Table I, appropriate to model compounds. For the linear complex, however, although the $^3(\pi \rightarrow \pi^*)$ states have energies in agreement with the experimental values, they are not directly dissociative,[18] and the $^3(d_\pi \rightarrow d_{z^2}^*)$ states which are dissociative[18] are at much

---

(32) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589–599.

(33) Weiss, K., unpublished results.

(34) Mataga, N.; Nishimoto, K. *Z. Phys. Chem.* (*Wiesbaden*) **1957**, *13*, 140–157.

(35) Rohmer, M.-M., unpublished results.

higher energies. On the other hand, for bent CO, the energy of the dissociative $^3(d_\pi \rightarrow d_{z^2}^*)$ states becomes comparable to that of $^3(\pi \rightarrow \pi^*)$ states with a value also consistent with the photodissociation experiments. As discussed previously,[18] the bent model may also be representative of model compounds as well as intact proteins. On the basis of these and previous results,[18] the observed low-energy triplet states in CO photodissociation are of $d_\pi \rightarrow d_{z^2}^*$ in nature. The intersystem crossing occurs following the initiation of dissociation by a singlet $d_\pi \rightarrow d_{z^2}^*$ transition consistent with the observed rapid spin conversion associated with the photolysis of HbCO.[36]

In conclusion, contrary to the recent reports,[3,4] our calculations of the triplet state energies of carbonylheme complexes for various ligand geometries show that the energy of the lowest triplet state is too high to accommodate a thermally populated paramagnetic state. The calculated energies of the $^3(d_\pi \rightarrow d_{z^2}^*)$ states in the bent geometry and $^3(\pi \rightarrow \pi^*)$ states in all geometries agree with the experimentally observed data in photodissociations by intermolecular triplet excitation transfer. Because of its dissociative nature, the $^3(d_\pi \rightarrow d_{z^2}^*)$ is identified as the state involved in the intersystem crossing during the photodissociation process.

Acknowledgment. The financial support from NSF Grant No. PCM 7921591 is gratefully acknowledged.

Registry No. H_6CO, 67684-33-7.

---

(36) Terner, J.; Stong, J. D.; Spiro, T. G.; Nagumo, M.; Nicol, M.; El-Sayed, M. A. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1313-1317.

Synthesis of Saccharides and Related Polyhydroxylated Natural Products. 3. Efficient Conversion of 2,3-*erythro*-Aldoses to 2,3-*threo*-Aldoses

Albert W. M. Lee, Victor S. Martin, Satoru Masamune,*
K. Barry Sharpless,* and Frederick J. Walker

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received February 18, 1982

The first communication[1a] of this series outlines a general approach to the synthesis of polyhydroxylated natural products of biological significance, covering a wide range of compounds from simple monosaccharides to the complex molecule palytoxin.[2] The approach basically consists of repetitive addition of a two-carbon unit on a proper starting aldehyde (**1**), creating two chiral hydroxymethylene centers (-*CHOH-) in each cycle of the sequence (Scheme I). The success of this strategy relies heavily upon both the efficiency and stereoselectivity attainable in the titanium-catalyzed asymmetric epoxidation[3] of the intermediate *E*- and *Z*-allylic alcohols (**2** and **3**), which, at the end of the sequence, should yield the acetonides of *erythro*- and *threo*-2,3-dihydroxy aldehydes (**4** and **5**), respectively.[4] Our preliminary examination of this sequence published recently[1] may be summarized as follows: (1) in all cases examined, the sequence leading to the 2,3-erythro products (**4**) through the *E* isomer **2** is satisfactory; (2) in contrast, the asymmetric epoxidation of **3** in the 2,3-threo series (**5**), when R* is chiral, often proceeds intolerably slowly and/or with low stereoselection. For this latter deficiency we now have an effective yet very simple remedy, which is described herein in the context of a unified route to the four possible D-pentoses. With this breakthrough our general approach stands on a solid foundation.

Compare the two structures **4** and **5**. These are epimeric only at C(2), which is α to the aldehyde group and thus epimerizable. From the expected stability of **5** relative to **4**, the latter readily obtainable epimer (**4**) (see above) would very likely be equilibrated to give a mixture enriched in **5**, which thus far has been of limited access. In this sense the selection of acetonide protection in **4** and **5** appears to be most appropriate. Not only is this protecting group definitely necessary to set up the interaction that provides the impetus for the desired epimerization, but at the same time the group would suppress the potential complication of a β elimination. This latter effect is anticipated because the acetonide group would maintain orthogonality between the enolate π system and the β-alkoxy substituent[5] (see **6** and **7** in Scheme I). This analysis of the problem has proven valid.

Thus, treatment of **4a-c** with potassium carbonate in methanol at 25 °C for 2 h effects smooth epimerization, providing the corresponding threo isomers **5a-c**, respectively (**5**:**4** = 20:1, Table I). These examples represent the tetrose, pentose, and hexose series. Incorporation of this critical epimerization technique in our general approach now leads to the satisfactory completion of the pentose synthesis.

In Scheme II, compound **8**, which was obtained earlier from **1a** through **2a**, undergoes ring opening[1] to provide **9**, which is converted to the corresponding acetonide **10** under the kinetic acetonation conditions originally developed by Horton et al.[6] Note that the acetonide present in the R group of **9** remains intact during this transformation. Reaction of **10** (0.81 mmol in 10 mL of toluene) with diisobutylaluminum hydride (1.3 mmol, 1 M in toluene) at -78 °C for 1.5 h provides, after aqueous workup and bulb-to-bulb distillation, a product (**11**) (86% yield) shown to be a ribose derivative by comparison with an authentic sample.[7] This reaction proceeds virtually without epimerization.[8] The aldehyde **11** along with the three other aldehydes described below shows a marked proclivity for becoming hydrated[8] and thus exists in two forms. Since a mixture of the aldehyde and its hydrate is difficult to analyze for diastereometric purity, further conformation has been made through the corresponding hydroxy compound, which is readily obtained from **11** by sodium borohydride reduction. Compound **10** is also converted into the C(2) epimer of **11**. Thus, treatment of **10** (0.065 mmol) with potassium carbonate (0.22 mmol) in methanol (0.5 mL) at 25 °C for 2 h causes hydrolysis of the acetoxythioacetal group and epimerization at the C(2) center to give a mixture of aldehydes **12** and **11** in a 98:2 ratio,[8]

---

(1) (a) Katsuki, T.; Lee, A. W. M.; Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Walker, F. J. *J. Org. Chem.* **1982**, *47*, 1373. (b) Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Viti, S. *Ibid.* **1982**, *47*, 1378.

(2) (a) Hirata, Y.; Uemura, D.; Ueda, K.; Takano, S. *Pure Appl. Chem.* **1979**, *51*, 1875. (b) Uemura, D.; Ueda, K.; Hirata, Y.; Naoki, H.; Iwashita, T. *Tetrahedron Lett.* **1981**, *22*, 1909, 2781 and references quoted therein. (c) Scheuer, P. J.; Moore, R. E. *Science (Washington, D.C.)* **1971**, *172*, 495. (d) Moore, R. E.; Bartolini, G. *J. Am. Chem. Soc.* **1981**, *103*, 2491.

(3) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.

(4) Of the two stereoisomers obtainable from each of **2** and **3**, only one for each series is shown in Scheme I.

(5) (a) Naef, R.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1981**, 1030. (b) Schaffer, R. *J. Am. Chem. Soc.* **1959**, *81*, 5452. (c) Williams, D. T.; Jones, J. K. N. *Can. J. Chem.* **1964**, *42*, 69. (d) Horton, D.; Jewell, J. S.; Just, E. K.; Wander, J. D. *Carbohydr. Res.* **1971**, *18*, 49. (e) Jarrell, H. C.; Szarek, W. A.; Jones, J. K. N.; Dmytraczenko, A.; Rathbone, E. B. *Ibid.* **1975**, *45*, 151. (f) Seebach, D,; Hungerbühler, E. "Modern Synthetic Methods 1980": Scheffold, R., Ed.; Salle and Sauerland-Verlag: Frankfurt and Aaron, 1980, and references cited therein. (g) See also: Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734, 736, 738.

(6) Fanton, E.; Gelas, J.; Horton, D.; Karl, H.; Khan, R.; Lee, C.-K.; Patel, G. *J. Org. Chem.* **1981**, *46*, 4057.

(7) Sodium borohydride reduction of **11** gave (2,3:4,5-diisopropylidene ribitol ($[\alpha]^{27}_D$ +7.0° (*c* 0.96, EtOH) which was identical (^1H NMR, IR, TLC, GLC, $[\alpha]_D$) with a sample prepared by kinetic acetonation[6] of 2,3-isopropylidene ribitol (see: Hughes, N. A.; Speakman, P. R. K. *Carbohydrate Res. I* **1965**, 171). Compound **12** and its $NaBH_4$ reduction product ($[\alpha]^{27}_D$ +12.2° (*c* 0.7, EtOH)) were identical in all respects with 2,3:4,5-diisopropylidene arabinose and its corresponding pentitol prepared from D-arabinose, respectively (see: Zinner, H.; Wittenburg, E.; Rembarz, G. *Chem. Ber.* **1959**, 1614). The lyxose series (**14**) was correlated by preparation of lyxitol pentaacetate ($[\alpha]^{22}_D = +40.5°$ (*c* 1.8, EtOH)) as previously described (see ref 1a), and finally the stereochemistry of the xylose series (**13**) follows from a process of elimination.

(8) The ratio of epimers was determined by integration of NMR spectra and GLC analysis of the sodium borohydride reduction products [i.e., the (2,3)-(4,5)-diisopropylidene-1-pentitols] of **14**, **13**, **12**, and **11** [retention times 16.1, 15.4, 13.4, and 12.6 min, respectively, 30 M fused silica capillary column, Carbowax 20 M (J & W Scientific, Inc.) 120 °C for 4 min, then program rate of 8 °C/min]. This observed high ratio (98:2) is likely due to the relative stability of the two methyl hemiacetals that form from **12** and **11** in methanol. We thank Professor W. R. Roush for this suggestion.

0002-7863/82/1504-3515$01.25/0