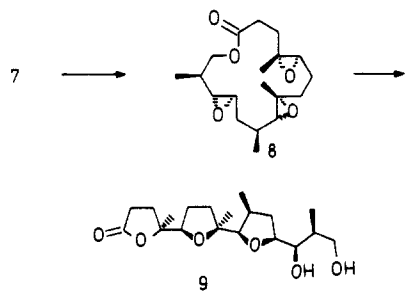
Scheme III



alkylation (stereoselection ca. 20:1),[4] and ester enolate Claisen rearrangement[5] via the *Z*-enol silyl ether separates the two asymmetric centers to give **3**. Stereocontrol in the rearrangement sequence was modest yielding a 4:1 mixture of diastereomers as a result of production of both *Z* and *E* ketene acetals (4:1) immediately prior to the rearrangement step. The identity of the major product as **3** was established by its conversion to *meso*-2,6-dimethylheptane-1,7-diol.[6] Standard Claisen methodology via **4** and **5** gave the triene **6**.

To allow the two chiral centers of triene **6** to control the required epoxidations efficiently, conversion to the corresponding 16-membered macrolide was carried out via the Mukaiyama procedure[7] (1 mM in CH_3CN, reflux, 1 h) yielding **7** in 68% yield (Scheme II). The macrolide was still a 4:1 diastereomeric mixture, but when it was epoxidized (MCPBA, $NaHCO_3$, CH_2Cl_2), a single triepoxide **8** was isolated by crystallization in 59% yield (74% based on diastereomerically pure **7**). Its X-ray structure is shown in Figure 1 and indicates that the two trisubstituted epoxides have the correct stereochemistry for monensin B and that the disubstituted epoxide is epimeric. The origin of the stereoselection observed is difficult to ascribe with confidence due to the kinetically controlled nature of the epoxidations. Furthermore, the flexibility of our 16-membered macrolide with its nine independent low-barrier torsional angles makes even a 60° resolution conformational analysis of the triene ground state impractical on a .34 MFLOP computer like a VAX 11/780.

To distinguish more clearly the product distribution from **7** itself, triepoxide **8** was deoxygenated ($N_2C(CO_2Me)_2$, $Rh_2(OAc)_4$, $PhCH_3$)[8] back to diastereomerically pure **7** and reepoxidized. High-field NMR showed a 20:1:1 mixture of triepoxides and demonstrates that the triepoxidation is highly stereoselective for **8**.

Although our triepoxide differs stereochemically from monensin B at one of the three epoxides, its polycyclization behavior provides strong support for the feasibility of the polyepoxide cyclization approach to the polyether antibiotics. Thus when **8** was saponified and worked up with excess HOAc, spontaneous cyclization to crystalline **9** (mp 89–90 °C) occurred in 94% yield.[9] The tricyclic structure shown was confirmed by X-ray crystallography (Scheme III).

To use such a scheme for natural ionophore synthesis, it will be necessary to alter the conformation of the macrocyclic triene and this will be the subject of further papers.[10]

Supplementary Material Available: Positional data and thermal parameters for crystal structures **8** and **9** (9 pages). Ordering information is given on any current masthead page.

(4) Frater, G. *Helv. Chim. Acta* **1979**, *62*, 2825.
(5) Ireland, R. E.; Mueller, R. H.; Willard, A. F. *J. Am. Chem. Soc.* **1976**, *98*, 2868.
(6) Still, W. C.; Darst, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 7385.
(7) Mukaiyama, T.; Usui, M.; Saigo, K. *Chem. Lett.* **1976**, *49*.
(8) Martin, M. G.; Ganem, B. *Tetrahedron Lett.* **1984**, 251.
(9) Triepoxide **8** (39 mg) in 5.0 mL of 1:1 MeOH/H_2O (0 °C) was treated with 2.0 mL of 0.1 N aqueous NaOH and stirred for 3 h. Acetic acid (2.0 mL) was added with the mixture was stirred (25 °C) until the starting material was consumed (ascertained by TLC). Partitioning between CH_2Cl_2 and saturated $NaHCO_3$ followed by flash chromatography on silica gel gave crystalline **9** (40 mg, 94%, mp 176 °C).
(10) This work was supported by NIH Grant HL25634.

Epoxidation of Unsaturated Macrolides: Stereocontrolled Routes to Ionophore Subunits

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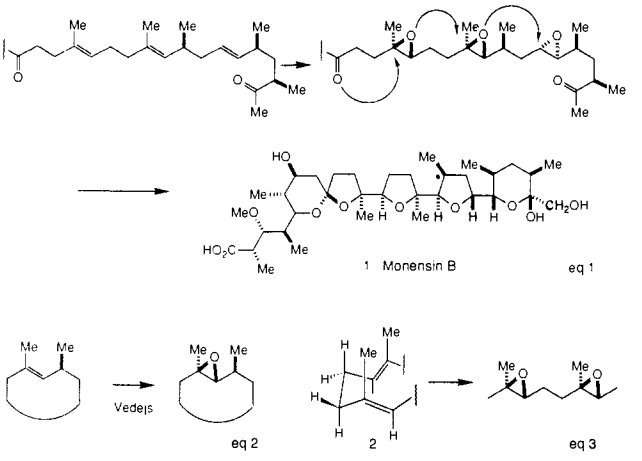
There has been considerable interest in the chemistry and biology of the polyether class of ionophores.[2] Recent studies on the biosynthesis of these materials by Cane, Celmer, and Westley led to the proposal that ether ring formation proceeds via polyene epoxidation and subsequent epoxide ring opening (eq 1).[3]



Nonbiological methods to mimic this process in a direct manner must address the absence of polar "directing" functionality[4] (e.g., hydroxyl substituent) in the vicinity of the olefin. One such method has emerged from a combination of studies on the conformational preferences and stereoselective reactions of macrocycles[5] and the directing property of a methyl substituent at allylic positions of unsaturated macrocycles.[6] In the latter study Vedejs and Gapinski reported that the epoxidation of an olefin containing the substitution pattern shown in eq 2 provided a single epoxide with the indicated stereochemistry. To address the problem of ionophore synthesis, we reasoned that a macrocycle containing a 1,5-diene could adopt the local conformation **2** (eq 3) that is free of torsional strain. Peripheral epoxidation[5] would result in the preferential formation of the *syn*-bisepoxide, a structural unit contained within the putative biogenetic intermediate. Herein we report on several applications of these principles that employ macrolides as templates

(1) Author to whom correspondence concerning X-ray crystallographic analysis should be addressed.
(2) *Polyether Antibiotics: Naturally Occurring Acid Ionophores*; Westley, J. W., Ed.; Marcel Dekker: New York, 1983; Vol. 1–2.
(3) (a) Cane, D. E.; Celmer, W. D.; Westley, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 3594. For experimental support in the specific case of monensin A, see: (b) Cane, D. E.; Liang, T.-C.; Hasler, H. *J. Am. Chem. Soc.* **1982**, *104*, 7274.
(4) Reviews of hydroxyl-directed epoxidation of olefins: (a) Berti, G. *Top. Stereochem.* **1973**, *7*, 93. (b) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63. (c) Kishi, Y. *Aldrichimica Acta* **1980**, *13*, 23. (d) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2. (e) Sheldon, R. A. In *Aspects of Homogeneous Catalysis*; Ugo, R. Ed.; D. Reidel Publishing Co.: Dordrecht, Holland, 1981; Vol. 4, p 3. (f) Sharpless, K. B.; Finn, M. G. In *Asymmetric Synthesis*; Morrison, J. D., Academic Press: New York, 1985; Vol. 5, p 247. (g) Rossiter, B. E. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 193. For recent contributions, see: (h) Kobayashi, Y.; Uchiyama, H.; Kanbara, H.; Sato, F. *J. Am. Chem. Soc.* **1985**, *107*, 5541 and references cited therein.
(5) (a) Still, W. C.; Galynker, I. *Tetrahedron* **1981**, *37*, 3981. For recent applications of the strategy of "macrocyclic stereocontrol", see: Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* **1984**, *106*, 1148 and references cited therein.
(6) (a) Vedejs, E.; Gapinski, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 5058, and references cited therein. For a related observation, see: (b) Corey, E. J.; Weigel, L. O.; Chamberlin, A. R.; Cho, H.; Hua, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 6613.

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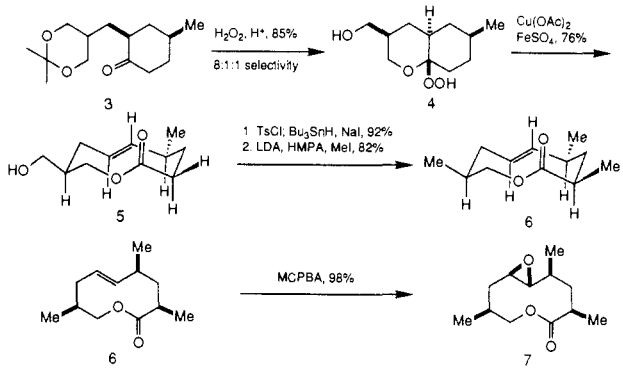
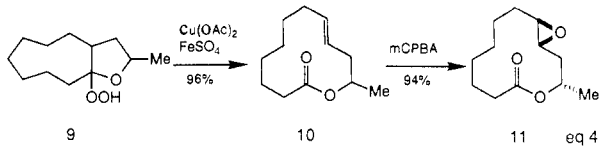
Scheme I



and have resulted in the preparation of subunits contained within the anticoccidial ionophore, monensin B (**1**).[7]

One method for the synthesis of unsaturated macrolides employs the iron/copper-promoted fragmentation of bicyclic peroxy ketals.[8] The fragmentation of **4** illustrates the positional selectivity and stereoselectivity that can be obtained in these reaction processes. The cis-disubstituted cyclohexanone (±)-**3**[9] is equipped with a prostereogenic carbon with paired ligands (diastereotopic alkoxymethyl groups). Low-temperature (−78 °C) peroxyketalization proceeded with diastereotopic group selectivity to afford three oxadecalins in an 8:1:1 ratio in 85% yield.[10] Fragmentation of the major product **4** under the standard conditions[8] provided macrolide **5** in 76% yield and with complete selectivity in the formation of the olefin.[11] ^{1}H NMR experiments (2D COSY and *J* value measurements) indicated this macrolide, and subsequent functionalized derivatives, exists in the expected chair–chair–chair conformation (**5**). The reduction of the hydroxymethyl substituent[12] to methyl was followed by a lactone alkylation[5] that proceeded with complete diastereoselection[13] to afford a macrolide (**6**) which contains the same methyl substitution pattern and stereochemistry as that found in the D and E rings of monensin. Upon treatment of **6** with MCPBA, a single epoxide **7** was produced in 98% yield (Scheme I). The stereochemical outcome of this reaction is in accord with the Vedejs model of local conformer control.[6] Although this compound contains the opposite epoxide configuration as that of the proposed biogenetic precursor (eq 1), our plan for the conversion of **7** into monensin entails a subsequent epoxide ring opening in the "unnatural" direction (E to D vs. the "natural" D to E ring) by employment of the lactonic carbonyl oxygen as a nucleophile. These studies are currently in progress.

An alternative route to an ionophore subunit was suggested by the fragmentation/epoxidation sequence outlined in eq 4.[14] In



this reaction the room temperature epoxidation of (±)-recifeiolide **10** resulted in the formation of the epoxide **11** (≥20:1), a result that may reflect the peripheral epoxidation of recifeiolide from a conformation analogous to **12** (**12′**). The use of this 12-membered macrolide template to prepare a B/C/D monensin B ring subunit is outlined in Scheme II. In this strategy, the stereogenic atom marked with an asterisk in compound **18** is responsible for controlling stereochemistry at the stereocenters of the B, C, and D rings in one step via remote internal asymmetric induction.

Scheme II

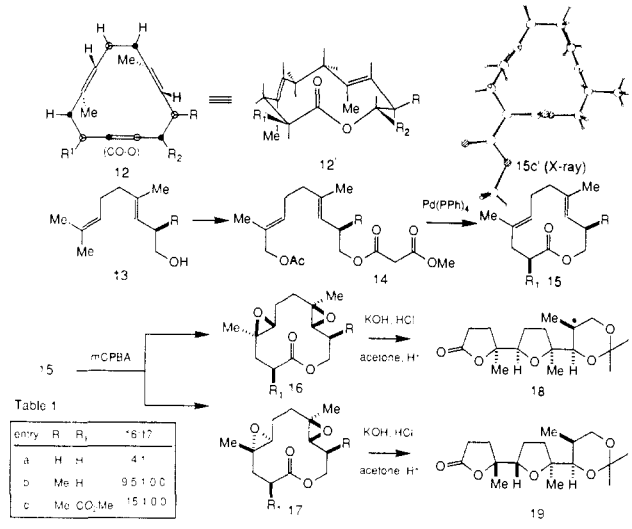


Table 1

entry	R	R_1	16:17
a	H	H	4:1
b	Me	H	9.5:1.0:0
c	Me	CO_2Me	15:1.0:0

Homogeraniol, upon treatment with Meldrum's acid and diazomethane, produced the mixed malonate that was oxidized according to the Sharpless procedure[15] and acetylated to afford **14a**. Alkylation of the *N,N*-dimethylhydrazone of homogeranial[16] (LDA, MeI), hydrolysis, and reduction afforded (±)-**13b** that was converted to **14b** by the same sequence employed with **13a**. Palladium-mediated macrocyclization[17] of **14a** and **14b** afforded the requisite macrolides (**14a** → **15** (R = H, R_1 = CO_2Me), 60% yield; **14b** → **15c**, 65% yield) that could be decarbomethoxylated by employment of Krapcho's conditions[18] (**15a**, 91% yield; **15b**, 93% yield). An important feature of the cyclization reaction **14b** → **15c** (vis-à-vis ionophore synthesis) concerns the near complete diastereotopic face selectivity observed in the internal alkylation of the malonyl enolate with the presumed π-allyl palladium intermediate, a result that is in accord with observations of Trost and Verhoeven in a related system.[17] The stereochemistry of **15c** (mp 68–70 °C) was suggested by NMR experiments and confirmed by X-ray crystallographic analysis (**15c′**). Interestingly, the macrolide conformation in the crystal is very similar to the conformation we had anticipated on the basis of molecular modeling (compare **15c′** and **12**).[19]

The oxidation of macrolides **15a–c** with mPCBA (−78 °C) proceeded stereoselectively to afford, as the major product, the bisepoxide that would arise from peripheral epoxidation of the crown conformation **12** (**12′**) (Table I). The 1,5-diene local conformation **2** (eq 3) depicted within **12** (**12′**) and observed in the crystal structure **15c′**, in combination with the Vedejs model,[6] provided the expectation that the required (with subsequent ring opening in the "natural" direction) *syn*-bisepoxide stereochemistry could be obtained. Substituents on the ring improved the selectivity from 4:1 (entry, a, Table I) to 9.5:1 (entry b) and 15:1 (entry c). The allylic methyl substituent proved a substantial stereocontrol device; only products in accord with the Vedejs model were obtained (**16b,c** and **17b,c**).[6] One-pot saponification and stereo-

(7) Related studies have been carried out by W. C. Still and A. G. Romero. The results of these studies are described in the preceding paper in this issue.

(8) (a) Schreiber, S. L. *J. Am. Chem. Soc.* **1980**, *102*, 6163. (b) Schreiber, S. L.; Liew, W.-F. *Tetrahedron Lett.* **1983**, *24*, 2363. (c) Schreiber, S. L.; Liew, W.-F. *J. Am. Chem. Soc.* **1985**, *107*, 2980. (d) Schreiber, S. L.; Hulin, B.; Liew, W.-F. *Tetrahedron*, in press.

(9) Prepared form 4-methylcyclohexanone by alkylation of the lithium enolate (LDA) with 2,2-dimethyl-5-(trifluoromethyl)sulfonyloxymethyl-1,3-dioxane and subsequent equilibration (NaOMe, MeOH, O °C, cis/trans = 20:1).[8d]

(10) All new compounds have been characterized by their ^{1}H NMR, ^{13}C NMR, IR, and MS data.

(11) A discussion on the selectivity observed in this and related reactions can be found in ref 8d.

(12) Ueno, Y.; Tanaka, C.; Okawara, M. *Chem. Lett.* **1983**, 795.

(13) For a description of the methods employed to determine stereochemistry, see supplementary material.

(14) Schreiber, S. L. Ph.D. Thesis, Harvard University, Cambridge, MA, 1981, Chapter 2.

(15) Umbreit, M. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 5526.

(16) Corey, E. J.; Enders, D. *Chem. Ber.* **1978**, *111*, 1337, 1362.

(17) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4743.

(18) Krapcho, A. P.; Weimaster, J. F.; Eldridge, J. M.; Jahngen, E. G. E.; Loevey, A. J.; Stephens, W. P. *J. Org. Chem.* **1978**, *43*, 138.

(19) Conformational analyses were performed with Professor Still's molecular mechanics program MODEL.

specific cyclization (KOH, then HCl in methanol) of **16b** and **17b** and subsequent acetonization afforded **18b** and **19b**,[20] respectively in 90–95% yield.[21] Stereochemical assignments could be made at this stage through a combination of high-field ^{1}H NMR experiments (NOE difference and J value measurements). The results of these analyses and the crystallographic data are included in the Supplementary Material.

Further studies directed toward the synthesis of polyether ionophores are currently under way.

Acknowledgment. This investigation was supported by the NIH (GM-30738), NSF (Presidential Young Investigator Award), and Pfizer Incorporated, to whom we are grateful. Fellowship support (for T.S.) was contributed by the Berlex Laboratories in the form of a Berlex Predoctoral Fellowship. We thank Dr. Simon K. Kearsley for the use of the UPLOT structure plotting package.

Supplementary Material Available: A description of the methods employed to determine stereochemistry including ^{1}H NMR, ^{13}C NMR, IR, and MS data and experimental procedures (11 pages). Ordering information is given on any current masthead page.

(20) Similar results were obtained in the cyclization and acetonization of **16a** and **17a** to provide **18a** and **19a**, respectively (β-methyl (of dioxane) = H).

(21) (a) Schultz, W. J.; Etter, M. C.; Pocius, A. V.; Smith, S. *J. Am. Chem. Soc.* **1980**, *102*, 7981. (b) Simmons, H. E.; Maggio, J. E. *Tetrahedron Lett.* **1981**, *22*, 287. (c) Paquette, L. A.; Vazeux, M. *Tetrahedron Lett.* **1981**, *22*, 291. (d) Dolle, R. E.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1985**, *107*, 1691. (e) Hoye, T. R.; Suhadolnik, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5312.

Synthesis and Structural Characterization of the First Phosphorus-Centered Baker–Figgis γ-Dodecametalate: γ-$Cs_5[PV_2W_{10}O_{40}]\cdot x H_2O$

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Contribution No. 3921, E. I. du Pont de Nemours & Co. Central Research & Development Department Experimental Station, Wilmington, Delaware 19898

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Phosphotungstates form a large class of heteropolyanions,[1] yet, surprisingly, only the α-form (Keggin structure) of dodecahedral $PX_yW_{12-y}O_{40}^{n-}$ species has been reported. In contrast, both the α- and β-Baker–Figgis isomers[2] of the corresponding silicates and germanates are known.[3] Recent work by us and others[4] has demonstrated the utility of lacunary (defect) polyoxoanions as precursors for the synthesis of specifically substituted larger polyanions; the fragments serve as ligands for other heteroatoms.

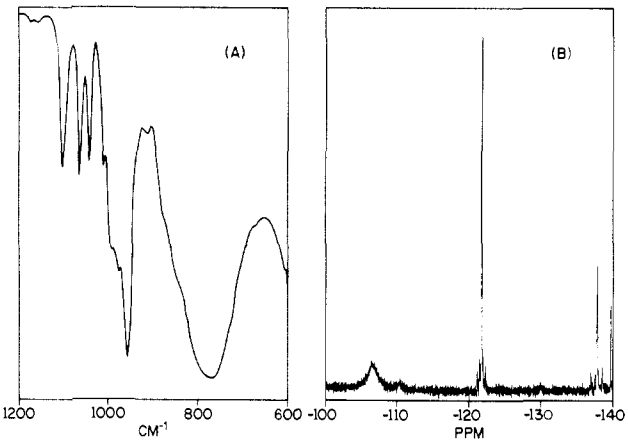

Figure 1. (A) IR spectrum (mineral oil mull) of γ-$Cs_5[PV_2W_{10}O_{40}]\cdot 6H_2O$. (B) ^{183}W NMR spectrum of 200 mg of $NaVO_3$, pH 2, 5 g of γ-$Li_5[PV_2W_{10}O_{40}]$ in 13 mL of D_2O, 5 °C, in a 20-mm vertical probe, 80 000 shots, total time 64 h, resolution enhanced to reveal $^2J_{WOW}$ satellites. The low-intensity resonance at −139.7 ppm is an unidentified pernicious impurity (ca. 2%, W_{10}).

Here we report the first Baker–Figgis γ-isomer[5] of a dodecahedral phosphotungstate species derived from the lacunary precursor[6] $Cs_7[PW_{10}O_{36}]$ and characterization by ^{183}W, ^{51}V, and ^{31}P NMR, IR spectroscopy, and X-ray crystallography.

Slow addition of up to 0.5 equiv of solid $Cs_7[PW_{10}O_{36}]\cdot xH_2O$ to a preformed solution of VO_2^+ at pH 0.8 yields an instantaneous precipitate[7] of γ-$Cs_5[PV_2W_{10}O_{40}]\cdot yH_2O$. Monitoring of the reaction by ^{51}V NMR shows a regular decrease in the intensity of the VO_2^+ resonance (−543.9 ppm) and the appearance of a weak resonance of essentially constant intensity (−570.3 ppm) due to the sparingly soluble product. Isolated solid shows a single ^{51}V NMR line[8a] (−547.1 ppm, $\Delta\nu_{1/2}$ = 112 Hz, pH 2.5, 30 °C) which is gradually replaced[8b] ($t_{1/2}$ ca. 7 h) by a pair of equal-intensity lines due[8c] to a β-$PV_2W_{10}O_{40}^{5-}$ species. In spite of the limited stability of the pure γ-compound, the material is substantially stabilized in the presence of an excess of VO_2^+. Suitable X-ray quality crystals were grown[9] from a 50 mol %, pH 2 solution of VO_2^+/γ-$Cs_5[PV_2W_{10}O_{40}]$ chilled to 0 °C. Microanalytical data were obtained on these crystals.

The IR spectrum (Figure 1A) is similar to that of other α-$PV_2W_{10}O_{40}^{5-}$ compounds,[4a,b] and the precursor $PW_{10}O_{36}^{7-}$. A notable difference is the decrease in frequency of the ca. 900-cm^{-1}

(1) See: Pope, M. T. "Heteropoly and Isopolymetalates", Springer-Verlag: New York, 1983, pp 65–72.

(2) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794–3797.

(3) See, for example: (a) Tézé, A.; Hervé, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 999–1002. (b) Hervé, G.; Tézé, A. *Inorg. Chem.* **1977**, *16*, 2115–2117. (c) Robert, F.; Tézé, A.; Hervé, G.; Jeannin, Y. *Acta Crystallogr., Sect. B* **1980**, *B36*, 11–15. (d) γ-$XV_2W_{10}O_{40}^{6-}$ (X = Si, Ge), which are analogous to the phosphorus species reported here, are mentioned in a meeting abstract but without details of synthesis or structure verification. Tézé, A.; Canny, J.; Leyrie, M.; Hervé, G. "Abstracts, Polyoxometallate Workshop"; St. Lambert-des-Bois, France, July, 1983.

(4) (a) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677–7687. (b) Domaille, P. J.; Watunya, G. *Inorg. Chem.*, submitted for publication. (c) Knoth, W. H.; Domaille, P. J.; Farlee, R. D. *Organometallics* **1984**, *4*, 62–68. (d) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286–4292. (e) Mossoba, M. M.; O'Connor, C. J.; Pope, M. T.; Sinn, E.; Hervé, G.; Tézé, A. *J. Am. Chem. Soc.* **1980**, *102*, 6864–6866. (f) Ortega, F.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 3292–3297. (g) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274–7277. (h) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *22*, 1006–1008. (i) Finke, R. G.; Droege, M. W.; Hutchinson, J. R.; Gansow, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587–1589. (j) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.*, in press.

(5) The γ-isomer reported here is not to be confused with the notation in a recent crystal structure: (a) Fuchs, J.; Thiele, A.; Palm, R. *Angew Chem., Int. Ed. Engl.* **1982**, *23*, 789–790. (b) A more recent interpretation of the X-ray data refutes the existence of the reported octahedral symmetry species: Evans, H. T.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 501–504. Our structure is a true Baker–Figgis γ-isomer based upon simultaneous 60° rotations of two adjacent M_3O_{13} units of the tetrahedral Keggin structure.[3d]

(6) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 1865–1867.

(7) $NaVO_3$, 1 g (8.2 mmol), was dissolved in 40 mL of hot water. Upon cooling, 3 M HCl was added dropwise to reduce the pH to 0.8. Small (10 mg) portions of $Cs_7[PW_{10}O_{36}]$ were added with vigorous stirring until a total of 12.5 g (3.6 mmol) had accumulated. After stirring for 30 min the solution was filtered to give 10.9 g of yellow powder (ca. 90%).

(8) (a) The position of the ^{51}V NMR resonance of the γ-isomer is pH-dependent. (b) Because of the stabilization by VO_2^+, rate parameters are dependent upon compound purity. The 7-h half-life was observed in unbuffered solution at pH 2.5. (c) The characterization of β-$PV_2W_{10}O_{40}^{5-}$ will be detailed in a forthcoming publication. Strong initial evidence is provided by the ^{51}V NMR spectrum. Two distinct lines (−544.4 and −555.2 ppm, pH 3.5, 30 °C) with non-Lorentzian line shapes are observed, indicating the presence of scalar coupling with $^2J_{VOV} \sim 20$ Hz. Confirmation is obtained by 2D ^{51}V COSY NMR.[4a]

(9) $NaVO_3$, 100 mg, was dissolved in 100 mL of water and adjusted to pH 2 with 3 M HCl. γ-$Cs_5[PV_2W_{10}O_{40}]\cdot xH_2O$, 5 g, was added and the mixture stirred for 30 min. Filtration through analytical filter aid produces a clear yellow solution which is chilled at 0 °C for 12 h to produce pale yellow crystals suitable for X-ray analysis. Prolonged chilling produces a total of 2.4 g of product which analyses for $Cs_5[PV_2W_{10}O_{40}]\cdot 6H_2O$. Calculated (Found): Cs, 19.6 (19.0); P, 0.92 (0.72); V, 3.01 (3.27); W, 54.3 (54.1); O, 21.8 (22.8); H, 0.36 (0.44); H_2O, 3.2 (3.2). Water content in the X-ray crystals will differ because of different drying procedures.

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